

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 14 May 1997		3. REPORT TYPE AND DATES COVERED Final report August 96 - Feb. 97	
4. TITLE AND SUBTITLE Multilayer Microlaminated Ceramic Thermal Barrier Coating				5. FUNDING NUMBERS F49620-96-C-0042	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Materials Modifications, Inc. 2929-P1 Eskridge Road Fairfax, VA 22031				8. PERFORMING ORGANIZATION REPORT NUMBER MMI-40-96	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Alexander Pechnik AFOSR/NA 110 Duncan Ave., Room B115 Bolling AFB DC 20332-8080				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release; Distribution is Unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report describes the Phase I effort to develop a new approach for applying micro-laminated thermal barrier coatings on superalloys through a sol-gel process. This new approach has better control of not only the process parameters but also the coating compositions and microstructures. Both thermal and mechanical characteristics of the coatings can be potentially optimized, and the coating will be more tolerant towards strain damage, have better thermal insulation and provide higher oxidation/corrosion resistance as compared with the existing single layer thermal barrier coatings. Cubic zirconia (yttria-stabilized-zirconia) can be coated through a sol-gel process onto bond coated superalloys. Zircon ($ZrSiO_4$) can be coated onto the yttria-stabilized-zirconia (YSZ) layer as a reinforcement layer. Cubic zirconia (yttria-stabilized-zirconia) can be coated onto the zircon layer. In Phase II, we will concentrate on optimization of the formulation, coating procedure and post treatment. Different coating techniques mentioned above will be used. A prototype coated turbine blade will be manufactured and undergo testing under simulated and actual conditions.					
14. SUBJECT TERMS thermal Barrier Coating, Yttria stabilized Zirconia, Sol-gel Processing, Gas Turbine				15. NUMBER OF PAGES 24	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL		

NSN

SF-298

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Multilayer Microlaminated Ceramic Thermal Barrier Coatings

Final Report

Submitted to

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AFOSR/NA
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110 Duncan Ave., Room B115
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Contract Number: F49620-96-C-0042
Period: August 1996 - February 1997

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1.0 Introduction

This report describes the Phase I effort to develop a new approach for applying micro-laminated thermal barrier coatings on superalloys through a sol-gel process. This new approach has better control of not only the process parameters but also the coating compositions and microstructures. Both thermal and mechanical characteristics of the coatings can be potentially optimized, and the coating will be more tolerant towards strain damage, have better thermal insulation and provide higher oxidation/corrosion resistance as compared with the existing single layer thermal barrier coatings.

Modern aircraft engine parts are subjected to increasingly severe thermal, mechanical and corrosive environments. Prior efforts have been focused on developing materials, which can withstand higher turbine inlet gas temperatures (which increases engine efficiency) and are more resistant towards harsh conditions such as marine environment and the use of low-grade fuel. This has seen the development of several generations of superalloys over the years. However, these alloys require cooling during the operational period and the practical temperature limits render further increases in inlet gas temperatures. Alternatively, the use of a thermal barrier coating can also improve the gas turbine efficiency through reduction of cooling airflow while maintaining the current gas temperatures.

Thermal barrier coatings consist of a thin layer of ceramic insulation applied to the external surface of metal components, such as combustion liners, transition pieces, nozzles and turbine blades. The reliability of the coating is critical, especially for the application in turbine nozzles and blades. Loss of the coating from such components can drastically shorten their life. There are a number of failure modes. The primary failure mode of thermal barrier coatings is spallation of the ceramic layer caused by the stresses during thermal cycling due to the thermal expansion coefficient mismatch between the coating and the substrate alloy.

There are currently two methods for applying thermal barrier coatings: 1) air plasma spray (APS) and 2) electron beam physical vapor deposition (EBPVD). The APS process generally produces coating with inferior mechanical properties but higher thermal barrier efficiency. The EBPVD technique, on the other hand, generally produces coatings with higher strain tolerance, smoother finishes and better erosion resistance. However, the corresponding thermal barrier efficiency of the coating by this approach is less and the coatings are expensive and less available. In this Phase I effort, we have focused on developing a new technique for applying micro-laminated thermal barrier coatings through a sol-gel approach.

2.0 Background

As gas turbine working temperatures are increased (for increasing efficiency), less refined fuels can be used (cheaper and available worldwide, but contain higher level of corrosive impurities). The need for operating in harsh conditions such as the marine environment also requires high temperature materials with excellent strength, toughness, oxidation and corrosion resistance, and cost effectiveness. Unfortunately, materials with all those excellent qualities are not available, and the most efficient way to meet the challenge is to use surface modification to improve the performance of existing materials to satisfy the requirements. Thermal-barrier and corrosion protective ceramic coatings have been utilized for providing long term surface stability for superalloys and other high temperature metallic components. The use of a thermal barrier coating enables an increase in turbine inlet gas temperature without an increase in the component metal temperature or a reduction in the coolant flow without decrease in turbine inlet gas temperature. The result is improved performance, efficiency and extenuated component life [1-4].

Assuming a hot spot gas temperature at 2280 °C, an inlet pressure of 3.85 MPa, the coolant temperature and pressure at 538 °C and 40.4 MPa, the calculated surface temperature of an uncoated blade at the suction side is 1055 °C. A 0.127 mm thick ceramic layer can decrease the metal temperature by 189 °C, and the temperature gradient across the ceramic would be almost 400 °C [5, 6]. The thermal insulating function of a thermal barrier coating can be best illustrated by the schematic of the temperature profile shown in Figure 1.

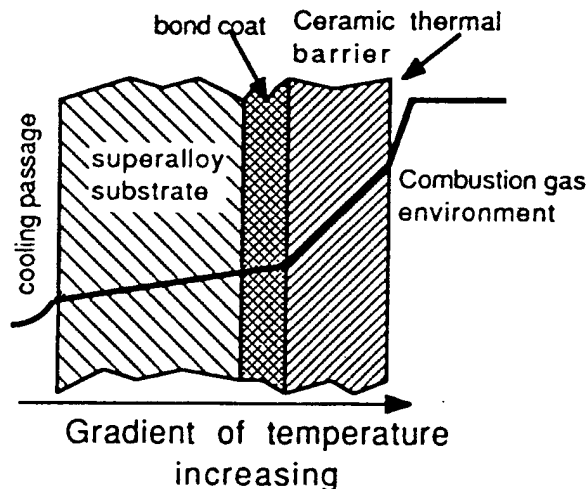


Figure 1. Schematic of temperature profile by thermal barrier coating.

Thermal barrier coatings are composite coatings with an inner metallic layer and an outer ceramic top-coat (Figure 1). The inner metallic layer, normally referred to as the bond coat, provides oxidation and corrosion protection by forming a protective oxide scale at the bond coat/ceramic interface, while the outer ceramic layer provides thermal

insulation due to its low thermal conductivity relative to the metal. The ceramic layer is generally made of zirconia based ceramics due to their superior thermal insulation properties, high melting temperatures, reasonable toughness and the acceptable thermal expansion mismatch with the metallic substrates. Although thermally insulative, this ceramic layer is generally porous and consists of cracks and does not greatly restrict the inward flux of oxygen or other corrosive gases. The bond coat is normally a metallic layer containing oxygen active elements such as Cr, Al and Y. The remainder is either Ni, Co, or the combination of these two elements. A typical MCrAlY bond coat (where M = Ni and/or Co) contains sufficient Al (6 to 9%) to provide oxidation protection by the formation of an Al_2O_3 scale. The bond coatings are physically deposited onto the substrate components. Air Plasma Spray (APS) and Electron Beam Physical Vapor Deposition (EBPVD) are the two most commonly used processes for applying bond coatings.

Currently, the APS and the EBPVD are also the two most commonly used techniques for applying the ceramic top layer of the thermal barrier coatings. It is obvious that the physical characteristics of ceramics and metals are dramatically different. The two techniques turn out to be not as successful in depositing ceramic layers as in applying metallic bond coatings. Although thermal barrier coatings have advantages to a point where they are in service in the turbine section of advanced gas turbine engines, the insufficient durability of the ceramic layers restricts the more extensive use of these coatings.

Figures 2 and 3 are cross section micrographs of typical $\text{ZrO}_2\text{-Y}_2\text{O}_3$ thermal barrier coatings made by the APS and the EBPVD. The ceramic top layer deposited by the APS has a porous structure (Figure 2), thus it has a higher thermal barrier efficiency. The microstructure of the layer, however, is not uniform, thus the coating has poor mechanical properties. On the other hand, the ceramic top layer deposited by the EBPVD has a columnar structure and appears denser than the plasma sprayed coating (Figure 3). This microstructure provides better mechanical properties and corrosion resistance than that of the APS sprayed layer. However, the corresponding thermal barrier efficiency is obviously reduced.

One primary failure mode of the thermal barrier coatings is spallation [8]. Examination of the failed components indicates that spallation occurs as a result of cracking in the ceramic layer parallel and adjacent to the metal-ceramic interface. The most common failure morphology of a thermal barrier coating involves spalling of the outer region of the ceramic while leaving a thin layer attached to the bond coat. This type of failure is attributed to the cyclic inelastic strain in the ceramics due to the thermal expansion mismatch between the ceramic top layer and the metallic substrate. Thermal expansion is the most common source of mismatch strains. There are three ways to reduce thermal expansion mismatch between coating and substrate.

1. Selecting coating materials with coefficient of thermal expansion (CTE) close to that of substrate.

2. Introducing transition layer of intermediate CTE between top coating and substrate.
3. Tailoring the microstructure of the coating.

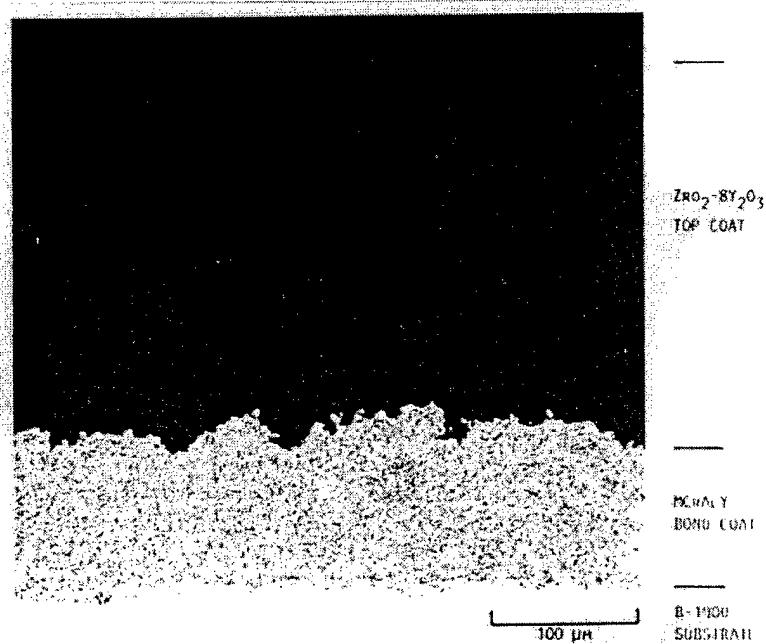


Figure 2. Cross section micrograph of a typical $ZrO_2-Y_2O_3$ thermal barrier coating deposited by air plasma spray (APS) [7].

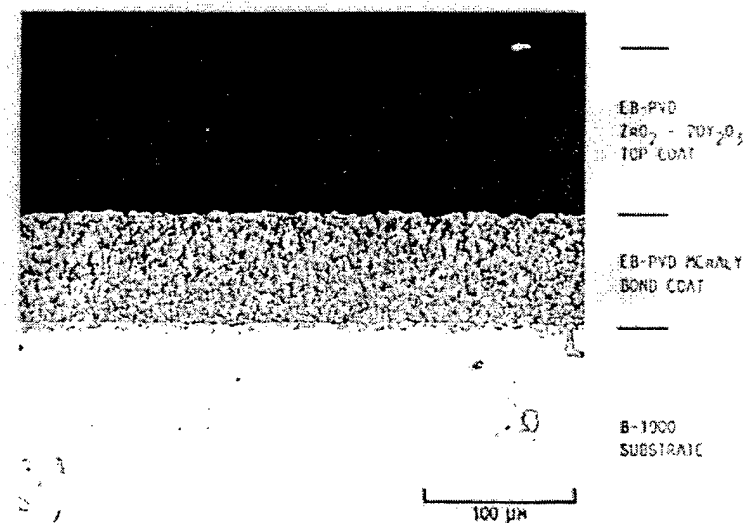


Figure 3. Cross section micrograph of a typical $ZrO_2-Y_2O_3$ thermal barrier coating deposited by electron beam physical vapor deposition (EBPVD) [7].

Current efforts have been focused on the first, and partially second, approach. One important reason for choosing yttria-stabilized zirconia (YSZ) as the top layer, aside from its good mechanical properties and corrosion resistance, is its high CTE. To some extent, the metallic bond coating also acts as a strain releasing transition layer in addition to its primary function for oxidation resistance. Although lacking adequate mechanical strength or toughness, certain oxides, such as cobalt oxide, magnesium oxide, nickel oxide and solid solutions containing these individual oxides, have very high CTE's, thus they are good candidates for strain releasing transition layers. Coatings for any application have a thickness restriction, and a multilayer coating demands reducing the thickness of the individual layer into micro or even nano scale. Exploring multilayer laminated ceramic coatings has been restricted by the difficulties in relationship to the uniform composition and thickness within such a small scale. Another important parameter for the thermal barrier coating is its microstructure. A porous structure, as compared to a dense one will have a higher thermal barrier efficiency and can better relieve thermal mismatch strains. However, large pores and nonuniform porous structures can significantly degrade the mechanical and thermal properties of the coating. Thus the microstructure of the individual layer also needs to be controlled.

Air Plasma Spray (APS) and Electron Beam Physical Vapor Deposition (EBPVD), currently used for applying thermal barrier coatings are two excellent techniques for thin layer metallic coatings. They can handle micro- (or even nano-, with EBPVD only) laminated metal coatings comfortably. Problems arise when the coating is ceramic in nature. The APS lacks control over coating thickness while both the APS and the EBPVD lack control over the coating microstructures. Simultaneous close control of microstructure as well as composition and uniform thickness within the individual layer is beyond their capability.

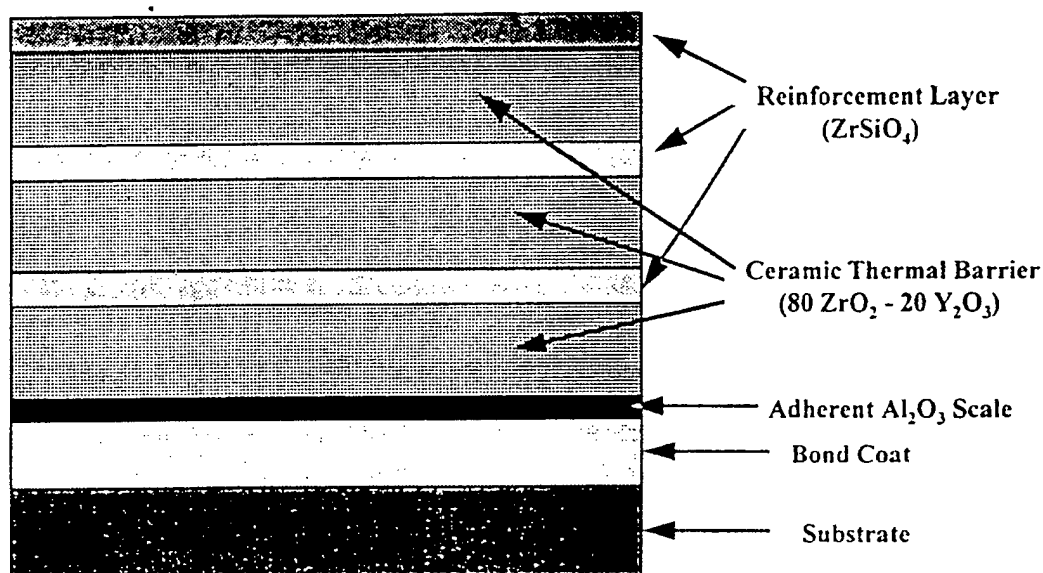
In this Phase I effort, we have attempted to utilize the strengths of sol-gel process, i.e. ease in handling complex composition and controllable microstructure, for multilayer micro-laminated ceramic thermal barrier coatings. The films developed through the sol-gel process showed good cohesion and adhesion, confirmed by tape tests.

3.0 Results of Phase I Effort

The principle of this Phase I research is that, by appropriately combining two or more materials, the functionality of a particular material system can be tailored and extended beyond what is possible with a single material system.

Thermal barrier ceramic coating with a multi-layer structural configuration will be more effective not only in terms of thermal insulation but also oxidation/corrosion protection. *A substantial increment in hot corrosion resistance is expected because a local damage in single laminate will have less negative impact compared with the situation where only one coating layer exists.* As a coating, however, its overall thickness is limited. A multilayer coating of limited overall thickness demands a micro- or even nano-laminated structure. To achieve sufficient thermal insulation, the key is to

A schematic of the multilayer micro-laminated coating structure is shown in Figure 4. The thickness of each individual laminate will be in the range between 0.5 to 5 μm . The porous yttria-stabilized zirconia (YSZ) layers will be responsible for thermal insulation. The ZrSiO_4 layers will act as reinforcement for improving coating integrity and mechanical strength. They will also function as oxygen barriers against oxidation and corrosion. A sol-gel process has been used for coating application due to its strength in microstructural control.

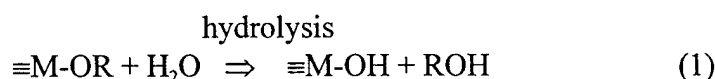


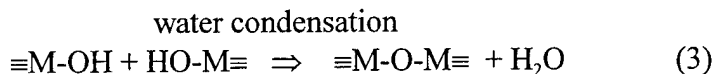
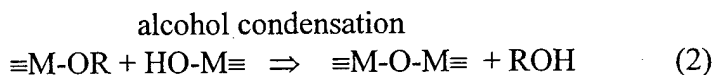
Our efforts were focused on the following specific objectives:

- Developing coating formulation,
- Establishing gel-coating sequence/procedure,
- Developing post gel-coating treatment process,
- Establishing relationships between coating microstructure and various processing parameters.

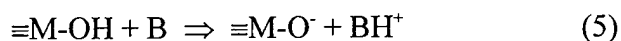
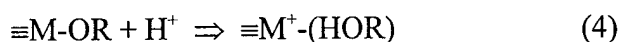
Sol-gel Synthesis of Coating Solutions

Sol-gel chemistry of the alkoxides can be generally described by the following three reactions.





where R is an alkyl group and M = Si, Y or Zr. Both acids and bases can be used as catalysts for the above reactions. The reaction kinetics are enhanced in the acid conditions by protonation of alkoxide which produces a good leaving group (4); and in the base conditions by producing strong nucleophiles via deprotonation of hydroxyl groups (5):



where R is an alkyl group and B is a Lewis base.

Metal alkoxides can react with moisture and CO₂ in air to form hydroxides and carbonates, respectively, thus complicating sol-gel processes. Normally, all procedures have to be carried out under an inert atmosphere (nitrogen or argon) to avoid the complication. Recently, it was found that the modification of a metal alkoxide to an M(OR)_x(OAc)_y type species, where R is an alkyl, OAc is an acetate group and x and y depend on the ratio of metal alkoxide and acetic acid, dramatically improves the stability of the precursor solutions [9]. The operations can be carried out under ambient conditions instead of under an inert atmosphere. We can treat metal alkoxides with glacial acetic acid to obtain acetoxylated precursors. This technique is very important as it can greatly lower the processing costs, especially for commercial applications. It can also help to circumvent the problem of premature hydrolysis of metal alkoxide precursors since under acidic conditions the hydrolyzed acetoxo type precursors can dissolve in excess water, thus making it possible to keep the precursor solutions for a long time without degradation.

Preparation of 20% Y₂O₃-80% ZrO₂ precursor dipping solution

1. A glove bag was set up under nitrogen atmosphere. Forty-eight grams of Zr butoxide (80% in butanol), which contains 0.1 mol of Zr, was dissolved in 57 ml of isopropanol in the glove bag. Yttrium isopropoxide (7.7 g of 95% Yttrium isopropoxide) was weighed and transferred into the reaction vessel. The total volume of the solution was about 200 mL.
2. The solution was refluxed for 2 h under nitrogen. After cooling down to room temperature, 76.7 g of acetic acid (10 times of the amount of Y and Zr) was added dropwise through an addition funnel. Acetic acid was added to acetoxylate some of

- the alkoxyl groups so that the dipping can be carried out in air instead of under an inert atmosphere. The resultant solution was refluxed for 2 h under nitrogen.
3. After the reaction vessel was cooled down to room temperature, water was added dropwise. A precipitate formed and re-dissolved upon adding more water. The total volume of water added was 180 mL (a fairly clear solution was obtained with addition of about 100 mL of water, but excess water was added).
 4. The total amount of the solution was 553 mL, which was the yttria-stabilized zirconia (YSZ) precursor solution, **Dipping Solution 1**.

Preparation of ZrSiO_4 dipping solution

1. Partial hydrolysis of tetraethyl orthosilicate (TEOS): 20.8 g (0.1 mole) of TEOS was dissolved in 300 mL of isopropanol, and 2.4 ml of water (0.13 mol, 1/3 equivalent of -OEt group) was added into the solution for hydrolysis. A few drops of 1.0 N nitric acid were added as catalyst. The solution (1) was warmed (40-50 °C) for three hours.
2. Preparation of Zr butoxide isopropanol solution: A glove bag was set up under nitrogen atmosphere. Forty-eight grams of Zr butoxide (80% in butanol), which contains 0.1 mol of Zr, was dissolved in 57 ml of isopropanol in the glove bag. The total volume was 100 mL (2). The reaction vessel was sealed under nitrogen and taken out of the glove bag.
3. The partially hydrolyzed isopropanol solution of TEOS (1) was added into the isopropanol solution of Zr butoxide (2) through an addition funnel under nitrogen. The resulting solution was refluxed for 2 h.
4. After cooling down to room temperature, 120 g of acetic acid (10 times excess relative to the amount of Zr and Si) was added dropwise into the solution through the addition funnel. Acetic acid was added to acetoxylate some of the ethoxyl groups so that the dipping can be carried out in air instead of under an inert atmosphere. The resultant solution was refluxed for 2 h under nitrogen.
5. After the reaction vessel was cooled down to room temperature, water was added dropwise. The solution became cloudy. Water was added continuously until a clear solution was obtained. The total volume of water was 80 mL.
6. The total amount of the solution was 538 mL, which was the ZrSiO_4 precursor solution, **Dipping Solution 2**.

Coating, Heat Treatment and Characterization

The development of a bond coating is not in the scope of the current investigation. However, pre-treating the bond coated substrate is a necessary step for further coating. The compositions of the bond coating are typically selected to form a stable alumina scale, which will be the final defense against oxidation, and it will also provide a suitable bond surface for the zirconia.

In this Phase I effort, three kinds of bond coated superalloys were used:

- 2 pin samples of IN 738 (3.5" x 1/4" ϕ) coated on one side with a NiCoCrAlY HVOF (High Velocity Oxygen Fuel) bond coat (similar to EBPVD TBC coating).
- 2 flat samples of IN738 (1" x 1/2" x 1/8") coated on one side with a NiCoCrAlY HVOF (High Velocity Oxygen Fuel) bond coat (similar to EBPVD TBC coating).
- 2 flat samples of IN738 (1" x 1/2" x 1/8") coated on one side with a NiCoCrAlY plasma bond coat.

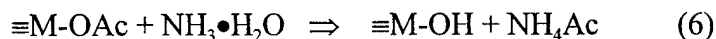
The substrates are all IN 738, and the bond coating composition is a NiCoCrAlY of GT-33/ATD 61 type.

Pin sample

The SEM pictures of the superalloy substrate and the bond coat are given in Figures 5 and 6, respectively. Thermal oxidation was used to generate the adherent Al_2O_3 scale, prior to applying the yttria-stabilized zirconia (YSZ) coatings. The bond-coated superalloy was heated in air to 1100 °C for 5 hours, and the color of the bond coat changed from gray to blue, and the SEM picture of the bond coat after heat treatment is shown in Figure 7. Spherical Al_2O_3 particles were formed, and this alumina layer provides oxidation protection to the underlying substrate.

The pretreated substrates were dipped in the YSZ precursor solution (dipping solution 1) and withdrawn at a constant slow rate. The "as synthesized" solution was used first, but was found to be too dilute. The concentrated solutions were used in all other experiments by reducing the volume of the dipping solutions to 1/10 of the original. The coated substrates were exposed to ammonia vapor overnight to facilitate development of the film.

The $\text{M}(\text{OR})_x(\text{OAc})_y$ type species in dipping solutions are quite stable. The addition of water to this precursor causes the hydrolysis of the alkoxy groups at a rate faster than the hydrolysis of the acetate groups. This hydrolyzed metal acetoxy type precursor $\text{M}(\text{OH})_a(\text{OAc})_b$ is soluble in excess water. When exposed to ammonia, the acetate groups in $\text{M}(\text{OH})_a(\text{OAc})_b$ are substituted by hydroxyl groups.



The condensation reactions (equations 2 and 3) are relatively fast, and a three-dimensional network is then formed.

The coated substrates were then heat-treated in air to 600 °C with a rate of 1 °C per minute. The samples were held at 600 °C for 1 hour and then cooled to room temperature. The SEM picture of the sample is given in Figure 8. The resulting YSZ layer consisted of blocks of YSZ from 1 or 2 μm to over 20 μm . The porous structure

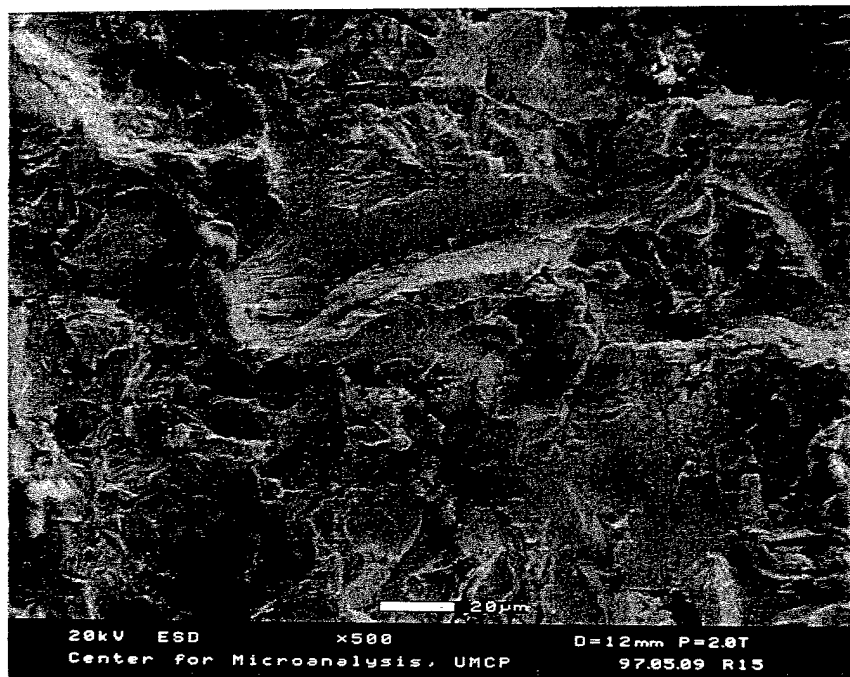


Figure 5. SEM micrograph of the superalloy substrate (pin sample) without any treatment (magnification 500).

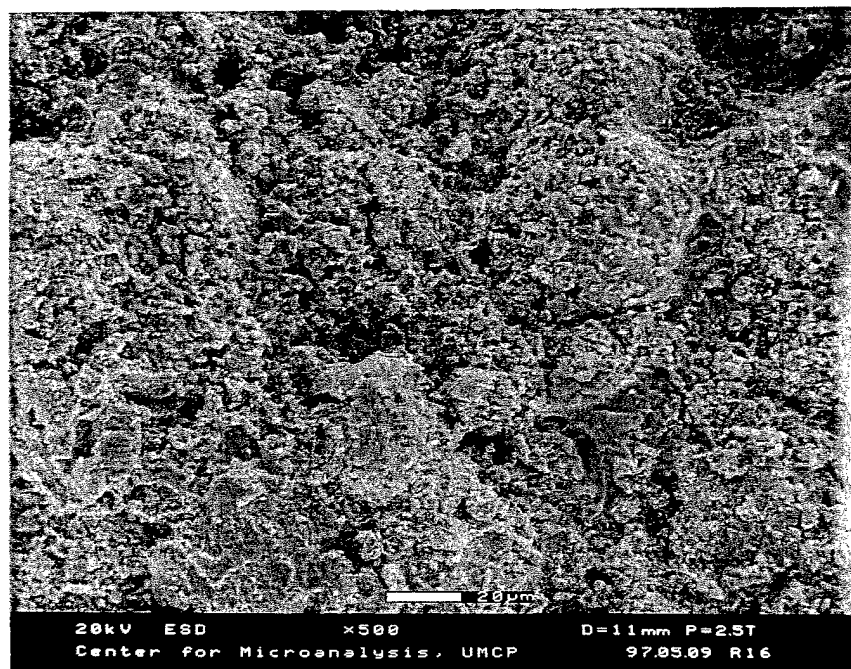


Figure 6. SEM micrograph of the bond coat of the pin sample prior to any treatment (magnification 500).

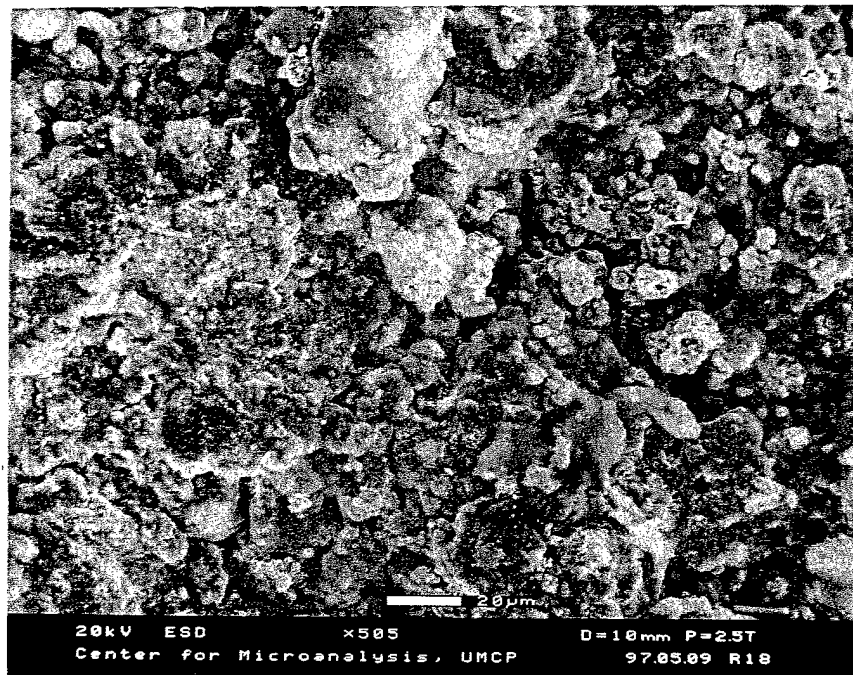


Figure 7. SEM micrograph of the bond coat (pin sample) after heat treatment at

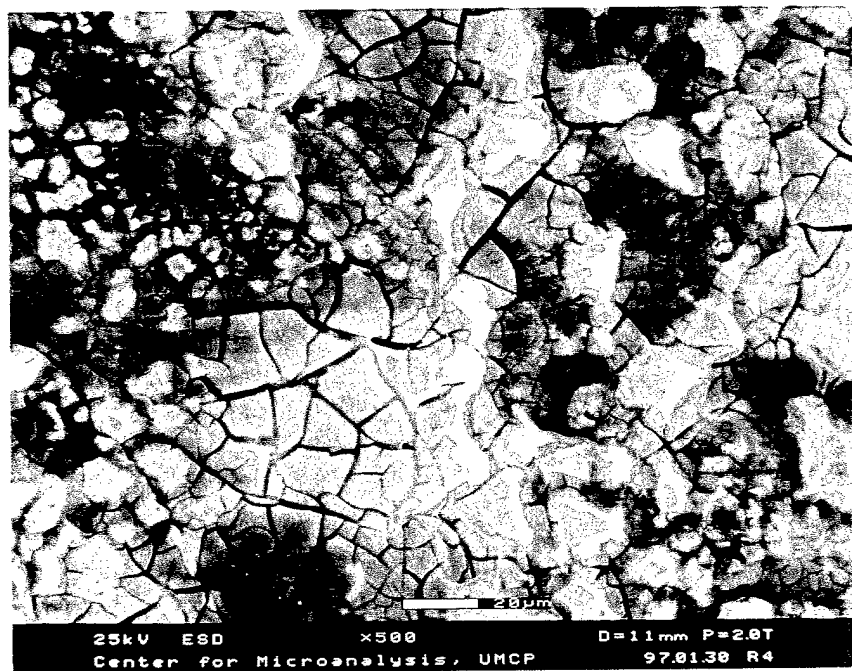


Figure 8. SEM micrograph of the YSZ film (pin sample) after heat treatment at 600 °C (magnification 500).

should provide good insulation. The thickness of the film was estimated about 1 to 2 μm , confirmed by micrometer measurement.

Flat sample with HVOF bond coat

As the yttria-stabilized zirconia (YSZ) layer is porous, oxygen can easily penetrate through the layer. The formation of Al_2O_3 scale and the YSZ can theoretically be accomplished simultaneously, which will reduce the processing cost. An experiment was carried out to verify the idea. The substrate was dip coated with the YSZ precursor solution (dipping solution 1) and heat-treated to 1100 $^{\circ}\text{C}$ in air with a rate of 5 $^{\circ}\text{C}$ per minute. The sample was held at 1100 $^{\circ}\text{C}$ for 1.5 h and cooled to room temperature. The uncoated part of the bond coat developed an Al_2O_3 scale, while the coated part developed a YSZ film. The SEM picture of the flat HVOF bond coat is given in Figure 9. The SEM pictures of the flat HVOF sample after heat treatment to 1100 $^{\circ}\text{C}$ without and with the YSZ coating are given in Figures 10 and 11, respectively.

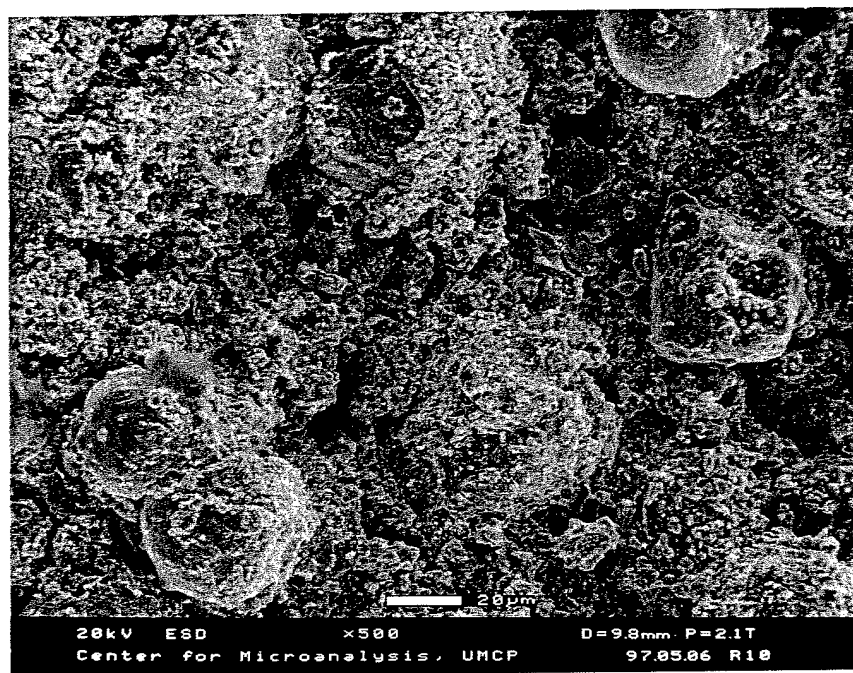


Figure 9. SEM micrograph of the HVOF bond coat without any treatment (magnification 500).

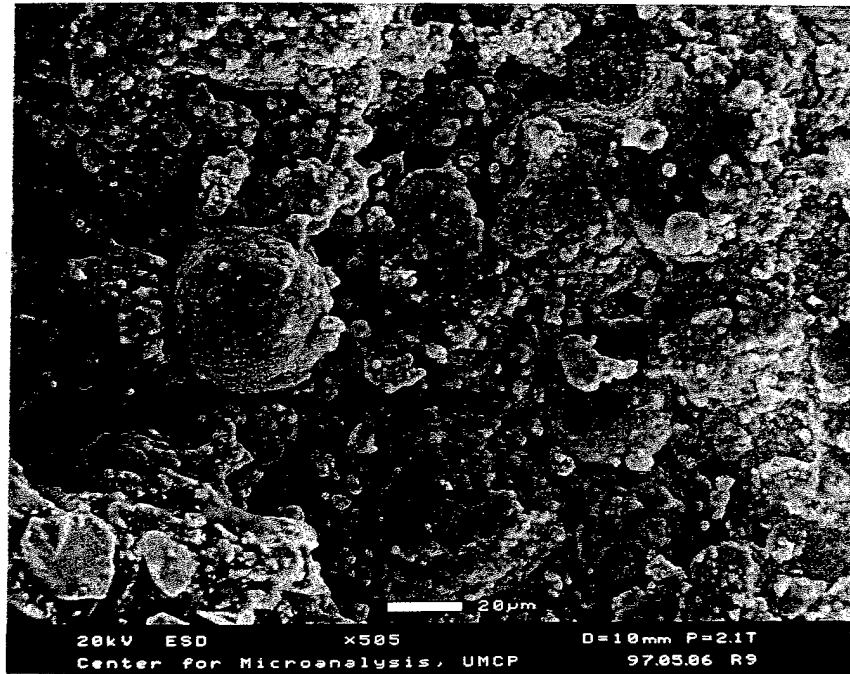


Figure 10. SEM micrograph of the flat HVOF bond coat after heat treatment to 1100 °C (magnification 500).

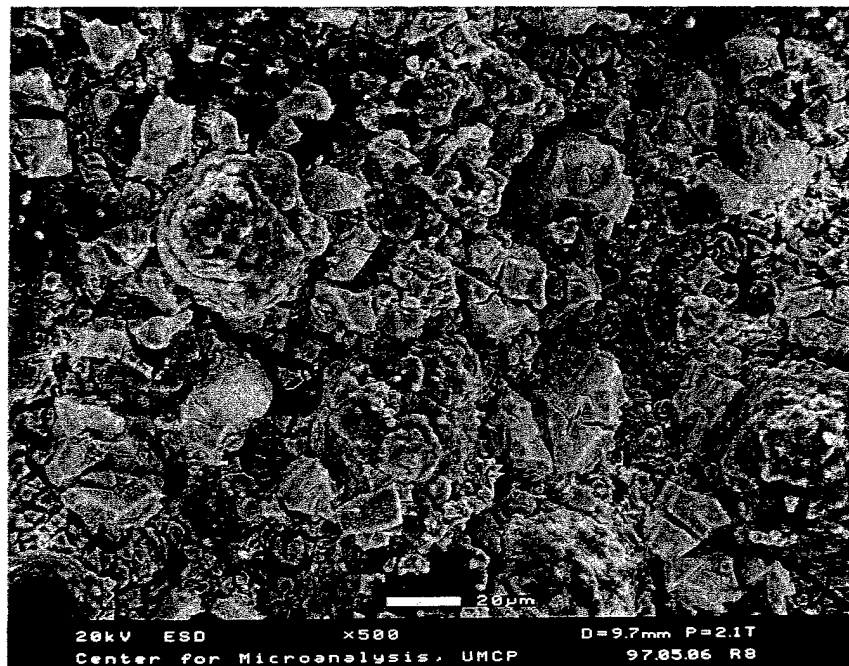


Figure 11. SEM micrograph of the YSZ film (flat HVOF sample) after heat treatment to 1100 °C (magnification 500).

Zirconia (ZrO_2) is polymorphic and undergoes two phase transitions, cubic to tetragonal at 2350 °C and tetragonal to monoclinic at 1170 °C. The latter transformation is accompanied by a 5% volume increase, which means that ZrO_2 has to be alloyed to stabilize one of the high temperature phases. An APD1700 Automated Powder Diffractometer with Cu radiation operated at 45 kV and 30 mA was used to identify the phase of YSZ films. The recorded XRD pattern is given in Figure 12. The observed peak intensity and position together with standard patterns of cubic zirconia ($a = 4.620 \text{ \AA}$, space group = Fm3m, labeled ZrO_2 27-997), two tetragonal zirconia ($a = 3.640 \text{ \AA}$, $c = 7.270 \text{ \AA}$, labeled ZrO_2 24-1164; $a = 5.120 \text{ \AA}$, $c = 5.250 \text{ \AA}$, labeled ZrO_2 17-923) are given in Figure 13. The coated film was clearly cubic zirconia, and the thickness was estimated to be 1-2 μm .

Flat sample with plasma bond coat

The superalloy sample with plasma bond coat was heat-treated to 1100 °C with a rate of 5 °C per minute. The sample was held at 1100 °C for 2 h and cooled to room temperature. The SEM picture of the alumina scale is given in Figure 14. The substrate was dip coated with the YSZ precursor solution (dipping solution 1) and exposed to ammonia overnight. The substrate was then heat-treated to 500 °C, which was enough for crystallization (Figure 15). The substrate was then dip coated with ZrSiO_4 precursor solution (dipping solution 2) and exposed to ammonia. The substrate was then again heat-treated to 500 °C, and a glassy phase of ZrSiO_4 was formed (Figure 16). The substrate was then coated with the dipping solution 1 again and exposed to ammonia overnight. After heat treatment to 500 °C, a zirconia film was formed (Figure 17). The APD1700 Automated Powder Diffractometer with Cu radiation operated at 45 kV and 30 mA was also used to identify the phase of YSZ films after 3rd coating. The recorded XRD spectrum is given in Figure 18. The observed peak intensity and position together with standard patterns of cubic zirconia ($a = 4.620 \text{ \AA}$, space group = Fm3m, labeled ZrO_2 27-997), two tetragonal zirconia ($a = 3.640 \text{ \AA}$, $c = 7.270 \text{ \AA}$, labeled ZrO_2 24-1164; $a = 5.120 \text{ \AA}$, $c = 5.250 \text{ \AA}$, labeled ZrO_2 17-923) are given in Figure 19. Cubic zirconia is clearly seen in the observed pattern, but the highest peak is due to the substrate, indicating high temperature heating does help crystallization of cubic zirconia.

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Sample: yao738 File: 050497.RD

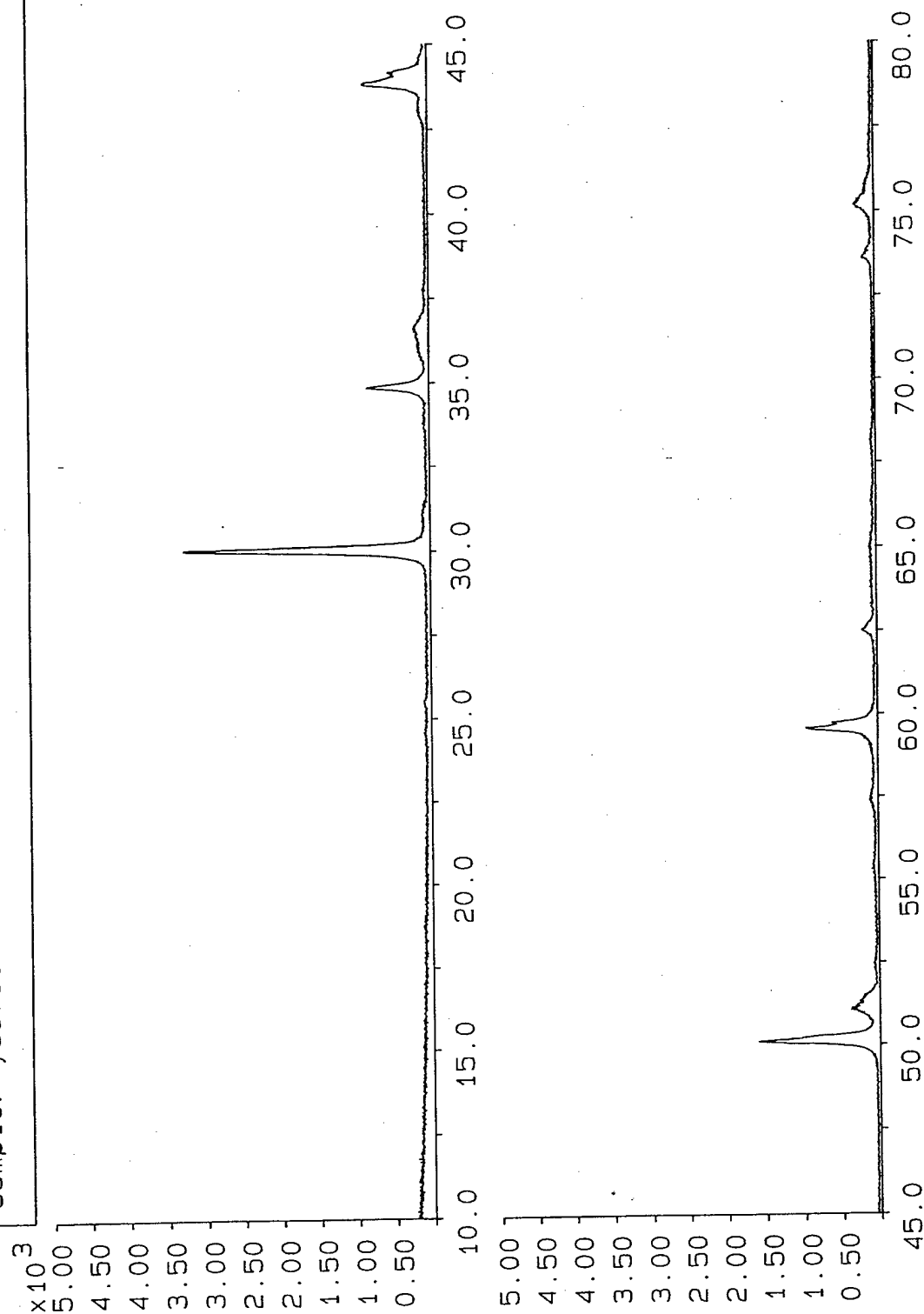


Figure 12. XRD pattern of the YSZ film (HVOF bond coat) after heat treatment at 1100 °C.

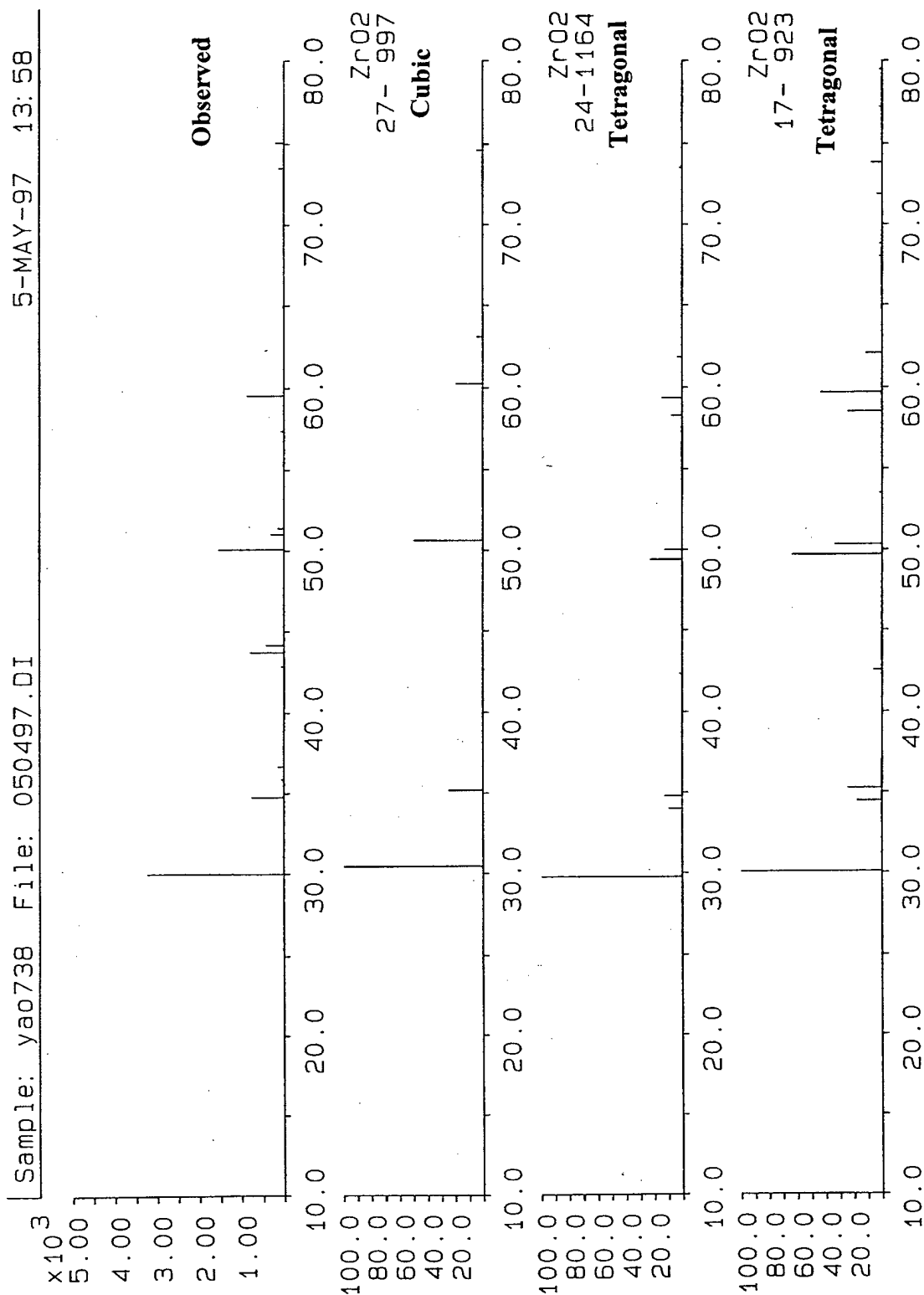


Figure 13. XRD patterns of the YSZ film (HVOF bond coat) after heat treatment at 1100 °C and some standard zirconia.

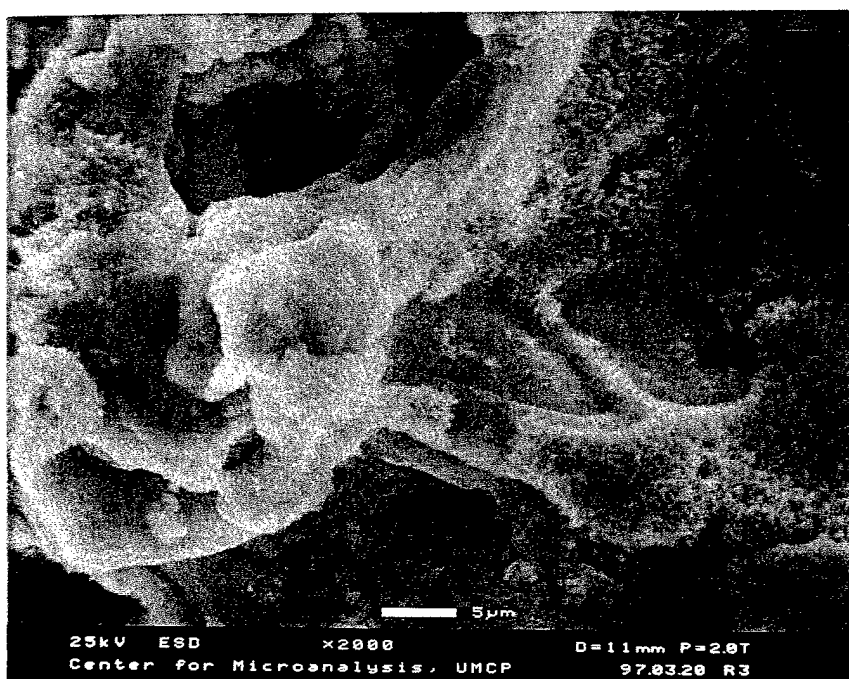


Figure 14. SEM micrograph of the plasma bond coat after heat treatment at 1100 °C (magnification 2000).

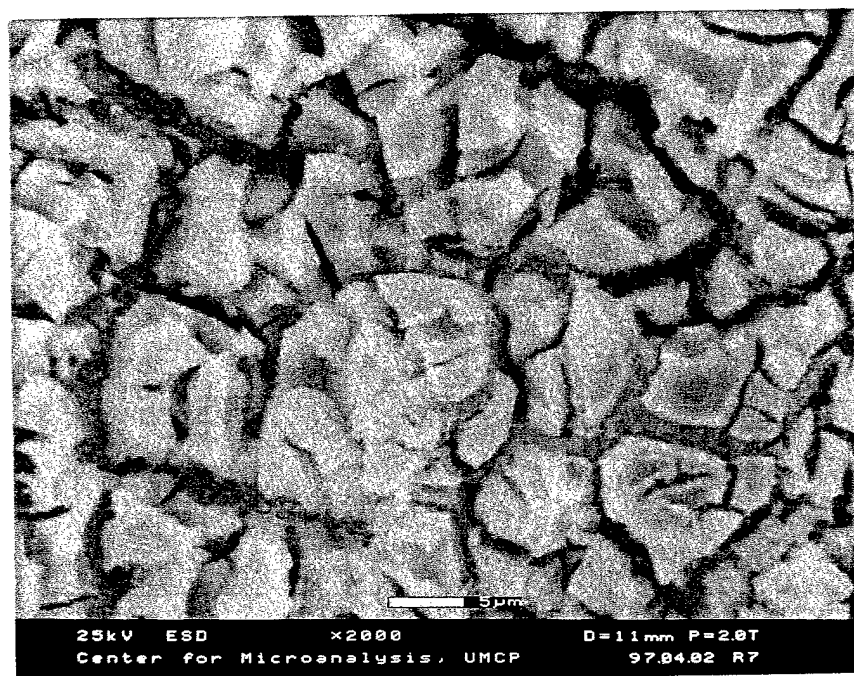


Figure 15. SEM micrograph of the YSZ film (plasma bond coat) heated to 500 °C after 1st coating (magnification 2000).

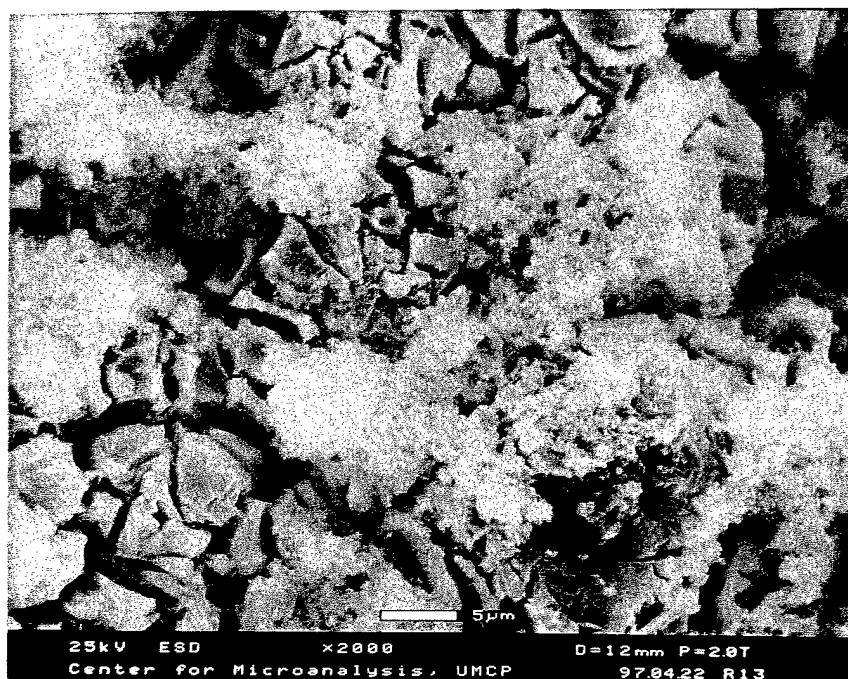


Figure 16. SEM micrograph of the ZrSiO₄ film (plasma bond coat) after heat treatment to 500 °C after 2nd coating (magnification 2000).

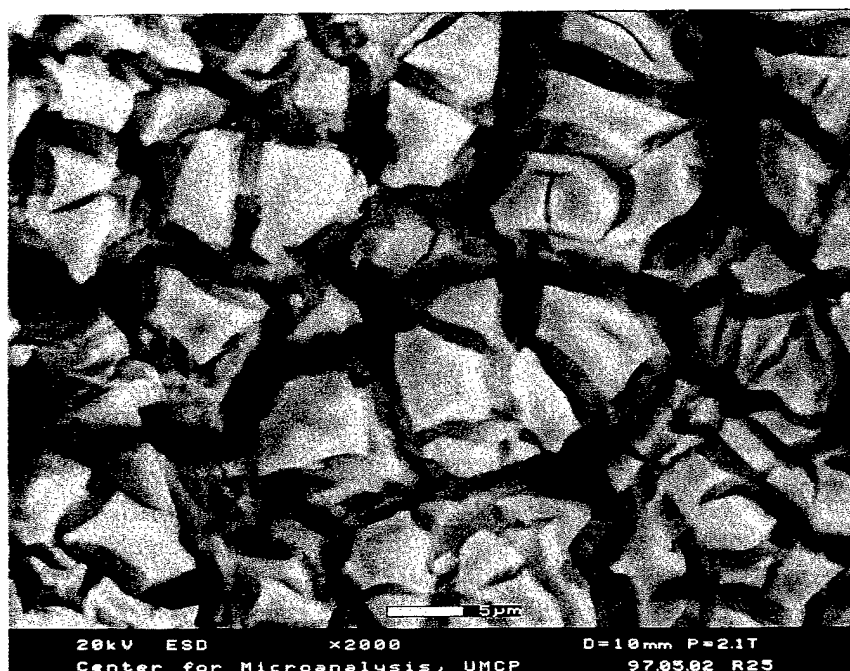


Figure 17. SEM micrograph of the YSZ film (plasma bond coat) after heat treatment to 500 °C after 3rd coating (magnification 2000).

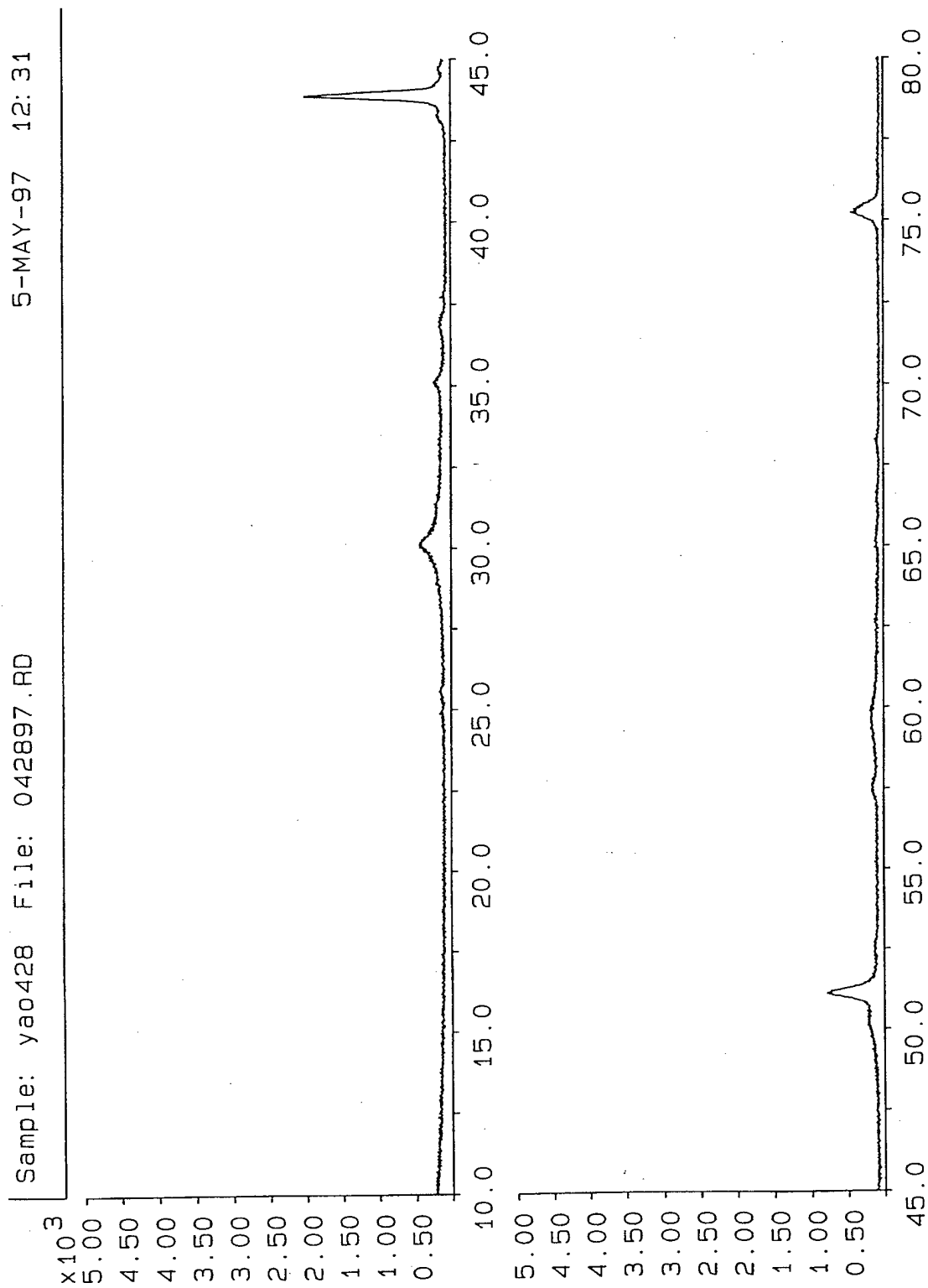


Figure 18. XRD pattern of the YSZ film (plasma bond coat) after 3rd coating (heat treatment at 500 °C).

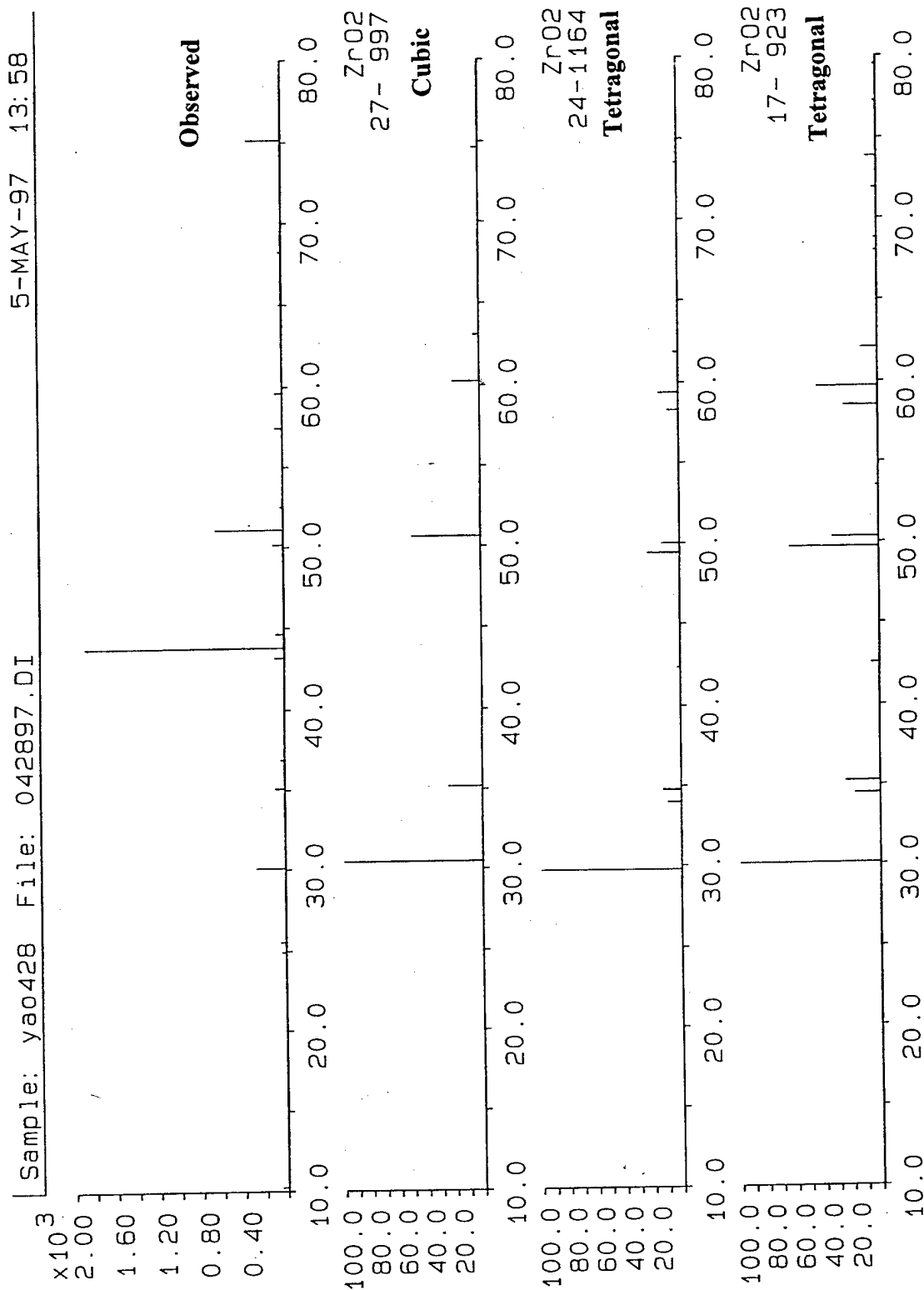


Figure 19. XRD patterns of the YSZ film (plasma bond coat) after 3rd coating (heat treatment 500 °C) and some standard zirconia.

4.0 Conclusions

This Phase I has demonstrated clearly the following:

- Cubic zirconia (yttria-stabilized-zirconia) can be coated through a sol-gel process onto bond coated superalloys. The films have very good adhesion and cohesion demonstrated by tape test. The films on the other side of the superalloy without bond coat peeled off very easily.
- Zircon (ZrSiO_4) can be coated onto the yttria-stabilized-zirconia (YSZ) layer as a reinforcement layer. The glassy phase may help to relieve the stress during thermal cycling.
- Cubic zirconia (yttria-stabilized-zirconia) can be coated onto the zircon layer. The feasibility of applying multilayer thermal barrier coating with micro-laminated structure through a sol-gel approach has been clearly demonstrated.
- The cubic zirconia films are stable at 1100 °C, which is close to the service temperatures of a turbine engine. The crystallization of the cubic zirconia can be achieved at 500 °C.
- All the objectives stated in the Phase I effort have been thus successfully completed.

Plans for Phase II

The development of this unique multilayer thermal barrier coating with micro-laminated structures through a sol-gel process has the potential to increase turbine-operating temperatures, reduce costs, and increase reliability. Even small increases in operating temperatures yield big payoffs in turbine performance, efficiency, and pollution reduction. The sol-gel process is very flexible for applications, and coatings can be applied through dip coating, spray coating, spin coating, roller coating, and brushing coating. It will be especially suitable for parts with complex geometry.

The experiences gained and the feedback obtained from the Phase I effort will be used as guidelines for further formulation refinement, process improvement, and product commercialization during Phase II.

In Phase II, we will concentrate on optimization of the formulation, coating procedure and post treatment. Different coating techniques mentioned above will be used. Extended tests of coating characteristics will be carried out. A new laser technique will be used to measure insulation of the films.

The feedback from the tests will be used to improve coating performance by microstructural modification such as sequence, thickness and porosity of the laminates. We will also explore other materials as reinforcement and oxygen barrier layers such as TiO_2 .

We will then manufacture a prototype coated turbine blade for extended ground testing under simulated conditions. Finally the prototype will undergo testing under actual conditions.

The path from Phase I to Phase II, to commercialization will be:

- Formulation and process refinement for production
- Coating characteristic evaluation
- Further improvement of formulation/process parameters based on evaluation feedback
- Prototype manufacturing and testing
- Analysis/identification/awareness of the strength/weakness of existing production process and competitors
- Demonstration of superior properties of our processes/products
- Patent rights
- Identification of markets for our products
- Detailed analysis of the potential for payoff
- Economics of scale-up of materials/equipment/personnel for large scale production
- Schematics of day to day operation
- Infrastructure build-up
- Development of marketing data.

Applications

The direct application of the technology developed in this SBIR effort will be multilayer, micro-laminated thermal barrier coatings on gas turbine components for high efficiency engines. This technology can also be used in a wide range of industries where protective coatings against corrosion and erosion for components used under severe conditions are essential. Other commercial applications include:

- scramjet and ramjet turbine component,
- reusable heat shields for reentry vehicle nosecones,
- flame nozzles
- water jet nozzles.

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This effort is funded by the Air Force Small Business Innovation Research Program.

Multilayer Microlaminated Ceramic Thermal Barrier Coatings

Final Report

Submitted to

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Contract Number: F49620-96-C-0042
Period: August 1996 - February 1997

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MMI - 40- 96

1.0 Introduction

This report describes the Phase I effort to develop a new approach for applying micro-laminated thermal barrier coatings on superalloys through a sol-gel process. This new approach has better control of not only the process parameters but also the coating compositions and microstructures. Both thermal and mechanical characteristics of the coatings can be potentially optimized, and the coating will be more tolerant towards strain damage, have better thermal insulation and provide higher oxidation/corrosion resistance as compared with the existing single layer thermal barrier coatings.

Modern aircraft engine parts are subjected to increasingly severe thermal, mechanical and corrosive environments. Prior efforts have been focused on developing materials, which can withstand higher turbine inlet gas temperatures (which increases engine efficiency) and are more resistant towards harsh conditions such as marine environment and the use of low-grade fuel. This has seen the development of several generations of superalloys over the years. However, these alloys require cooling during the operational period and the practical temperature limits render further increases in inlet gas temperatures. Alternatively, the use of a thermal barrier coating can also improve the gas turbine efficiency through reduction of cooling airflow while maintaining the current gas temperatures.

Thermal barrier coatings consist of a thin layer of ceramic insulation applied to the external surface of metal components, such as combustion liners, transition pieces, nozzles and turbine blades. The reliability of the coating is critical, especially for the application in turbine nozzles and blades. Loss of the coating from such components can drastically shorten their life. There are a number of failure modes. The primary failure mode of thermal barrier coatings is spallation of the ceramic layer caused by the stresses during thermal cycling due to the thermal expansion coefficient mismatch between the coating and the substrate alloy.

There are currently two methods for applying thermal barrier coatings: 1) air plasma spray (APS) and 2) electron beam physical vapor deposition (EBPVD). The APS process generally produces coating with inferior mechanical properties but higher thermal barrier efficiency. The EBPVD technique, on the other hand, generally produces coatings with higher strain tolerance, smoother finishes and better erosion resistance. However, the corresponding thermal barrier efficiency of the coating by this approach is less and the coatings are expensive and less available. In this Phase I effort, we have focused on developing a new technique for applying micro-laminated thermal barrier coatings through a sol-gel approach.

2.0 Background

As gas turbine working temperatures are increased (for increasing efficiency), less refined fuels can be used (cheaper and available worldwide, but contain higher level of corrosive impurities). The need for operating in harsh conditions such as the marine environment also requires high temperature materials with excellent strength, toughness, oxidation and corrosion resistance, and cost effectiveness. Unfortunately, materials with all those excellent qualities are not available, and the most efficient way to meet the challenge is to use surface modification to improve the performance of existing materials to satisfy the requirements. Thermal-barrier and corrosion protective ceramic coatings have been utilized for providing long term surface stability for superalloys and other high temperature metallic components. The use of a thermal barrier coating enables an increase in turbine inlet gas temperature without an increase in the component metal temperature or a reduction in the coolant flow without decrease in turbine inlet gas temperature. The result is improved performance, efficiency and extenuated component life [1-4].

Assuming a hot spot gas temperature at 2280 °C, an inlet pressure of 3.85 MPa, the coolant temperature and pressure at 538 °C and 40.4 MPa, the calculated surface temperature of an uncoated blade at the suction side is 1055 °C. A 0.127 mm thick ceramic layer can decrease the metal temperature by 189 °C, and the temperature gradient across the ceramic would be almost 400 °C [5, 6]. The thermal insulating function of a thermal barrier coating can be best illustrated by the schematic of the temperature profile shown in Figure 1.

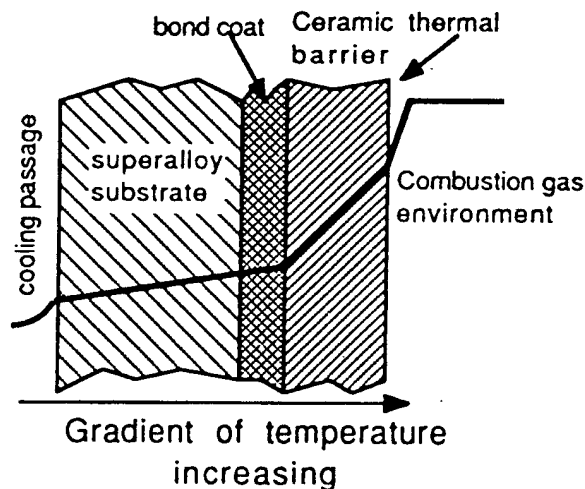


Figure 1. Schematic of temperature profile by thermal barrier coating.

Thermal barrier coatings are composite coatings with an inner metallic layer and an outer ceramic top-coat (Figure 1). The inner metallic layer, normally referred to as the bond coat, provides oxidation and corrosion protection by forming a protective oxide scale at the bond coat/ceramic interface, while the outer ceramic layer provides thermal

insulation due to its low thermal conductivity relative to the metal. The ceramic layer is generally made of zirconia based ceramics due to their superior thermal insulation properties, high melting temperatures, reasonable toughness and the acceptable thermal expansion mismatch with the metallic substrates. Although thermally insulative, this ceramic layer is generally porous and consists of cracks and does not greatly restrict the inward flux of oxygen or other corrosive gases. The bond coat is normally a metallic layer containing oxygen active elements such as Cr, Al and Y. The remainder is either Ni, Co, or the combination of these two elements. A typical MCrAlY bond coat (where M = Ni and/or Co) contains sufficient Al (6 to 9%) to provide oxidation protection by the formation of an Al_2O_3 scale. The bond coatings are physically deposited onto the substrate components. Air Plasma Spray (APS) and Electron Beam Physical Vapor Deposition (EBPVD) are the two most commonly used processes for applying bond coatings.

Currently, the APS and the EBPVD are also the two most commonly used techniques for applying the ceramic top layer of the thermal barrier coatings. It is obvious that the physical characteristics of ceramics and metals are dramatically different. The two techniques turn out to be not as successful in depositing ceramic layers as in applying metallic bond coatings. Although thermal barrier coatings have advantages to a point where they are in service in the turbine section of advanced gas turbine engines, the insufficient durability of the ceramic layers restricts the more extensive use of these coatings.

Figures 2 and 3 are cross section micrographs of typical $\text{ZrO}_2\text{-Y}_2\text{O}_3$ thermal barrier coatings made by the APS and the EBPVD. The ceramic top layer deposited by the APS has a porous structure (Figure 2), thus it has a higher thermal barrier efficiency. The microstructure of the layer, however, is not uniform, thus the coating has poor mechanical properties. On the other hand, the ceramic top layer deposited by the EBPVD has a columnar structure and appears denser than the plasma sprayed coating (Figure 3). This microstructure provides better mechanical properties and corrosion resistance than that of the APS sprayed layer. However, the corresponding thermal barrier efficiency is obviously reduced.

One primary failure mode of the thermal barrier coatings is spallation [8]. Examination of the failed components indicates that spallation occurs as a result of cracking in the ceramic layer parallel and adjacent to the metal-ceramic interface. The most common failure morphology of a thermal barrier coating involves spalling of the outer region of the ceramic while leaving a thin layer attached to the bond coat. This type of failure is attributed to the cyclic inelastic strain in the ceramics due to the thermal expansion mismatch between the ceramic top layer and the metallic substrate. Thermal expansion is the most common source of mismatch strains. There are three ways to reduce thermal expansion mismatch between coating and substrate.

1. Selecting coating materials with coefficient of thermal expansion (CTE) close to that of substrate.

2. Introducing transition layer of intermediate CTE between top coating and substrate.
3. Tailoring the microstructure of the coating.

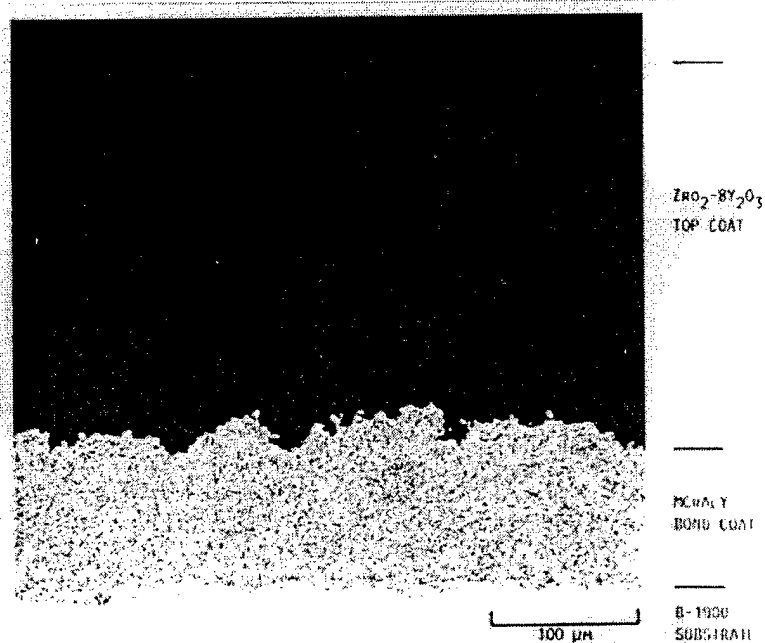


Figure 2. Cross section micrograph of a typical ZrO₂-Y₂O₃ thermal barrier coating deposited by air plasma spray (APS) [7].

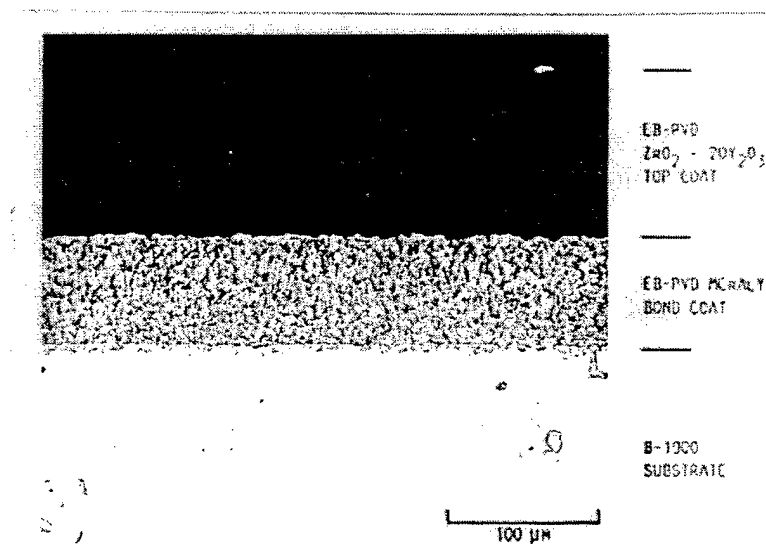


Figure 3. Cross section micrograph of a typical ZrO₂-Y₂O₃ thermal barrier coating deposited by electron beam physical vapor deposition (EBPVD) [7].

Current efforts have been focused on the first, and partially second, approach. One important reason for choosing yttria-stabilized zirconia (YSZ) as the top layer, aside from its good mechanical properties and corrosion resistance, is its high CTE. To some extent, the metallic bond coating also acts as a strain releasing transition layer in addition to its primary function for oxidation resistance. Although lacking adequate mechanical strength or toughness, certain oxides, such as cobalt oxide, magnesium oxide, nickel oxide and solid solutions containing these individual oxides, have very high CTE's, thus they are good candidates for strain releasing transition layers. Coatings for any application have a thickness restriction, and a multilayer coating demands reducing the thickness of the individual layer into micro or even nano scale. Exploring multilayer laminated ceramic coatings has been restricted by the difficulties in relationship to the uniform composition and thickness within such a small scale. Another important parameter for the thermal barrier coating is its microstructure. A porous structure, as compared to a dense one will have a higher thermal barrier efficiency and can better relieve thermal mismatch strains. However, large pores and nonuniform porous structures can significantly degrade the mechanical and thermal properties of the coating. Thus the microstructure of the individual layer also needs to be controlled.

Air Plasma Spray (APS) and Electron Beam Physical Vapor Deposition (EBPVD), currently used for applying thermal barrier coatings are two excellent techniques for thin layer metallic coatings. They can handle micro- (or even nano-, with EBPVD only) laminated metal coatings comfortably. Problems arise when the coating is ceramic in nature. The APS lacks control over coating thickness while both the APS and the EBPVD lack control over the coating microstructures. Simultaneous close control of microstructure as well as composition and uniform thickness within the individual layer is beyond their capability.

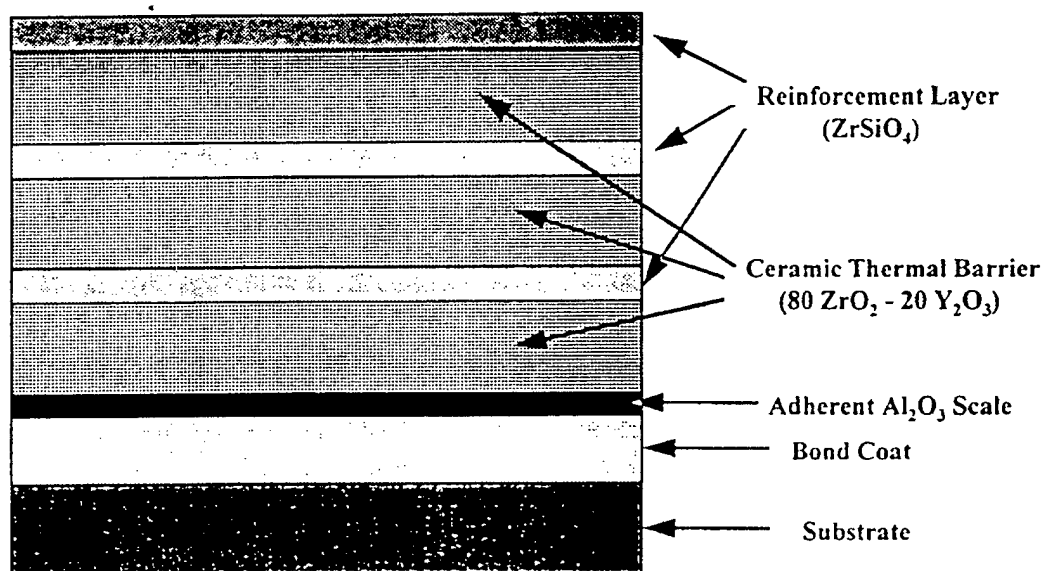
In this Phase I effort, we have attempted to utilize the strengths of sol-gel process, i.e. ease in handling complex composition and controllable microstructure, for multilayer micro-laminated ceramic thermal barrier coatings. The films developed through the sol-gel process showed good cohesion and adhesion, confirmed by tape tests.

3.0 Results of Phase I Effort

The principle of this Phase I research is that, by appropriately combining two or more materials, the functionality of a particular material system can be tailored and extended beyond what is possible with a single material system.

Thermal barrier ceramic coating with a multi-layer structural configuration will be more effective not only in terms of thermal insulation but also oxidation/corrosion protection. *A substantial increment in hot corrosion resistance is expected because a local damage in single laminate will have less negative impact compared with the situation where only one coating layer exists.* As a coating, however, its overall thickness is limited. A multilayer coating of limited overall thickness demands a micro- or even nano-laminated structure. To achieve sufficient thermal insulation, the key is to

A schematic of the multilayer micro-laminated coating structure is shown in Figure 4. The thickness of each individual laminate will be in the range between 0.5 to 5 μm . The porous yttria-stabilized zirconia (YSZ) layers will be responsible for thermal insulation. The ZrSiO_4 layers will act as reinforcement for improving coating integrity and mechanical strength. They will also function as oxygen barriers against oxidation and corrosion. A sol-gel process has been used for coating application due to its strength in microstructural control.



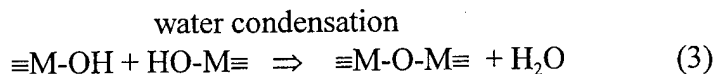
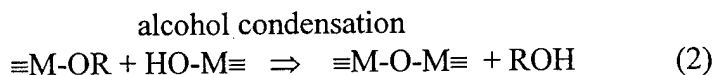
Our efforts were focused on the following specific objectives:

- Developing coating formulation,
- Establishing gel-coating sequence/procedure,
- Developing post gel-coating treatment process,
- Establishing relationships between coating microstructure and various processing parameters.

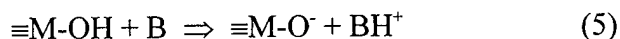
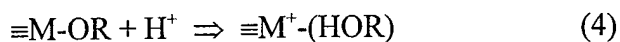
Sol-gel Synthesis of Coating Solutions

$$\text{hydrolysis}$$

$$\equiv\text{M-OR} + \text{H}_2\text{O} \Rightarrow \equiv\text{M-OH} + \text{ROH} \quad (1)$$



where R is an alkyl group and M = Si, Y or Zr. Both acids and bases can be used as catalysts for the above reactions. The reaction kinetics are enhanced in the acid conditions by protonation of alkoxide which produces a good leaving group (4); and in the base conditions by producing strong nucleophiles via deprotonation of hydroxyl groups (5):



where R is an alkyl group and B is a Lewis base.

Metal alkoxides can react with moisture and CO₂ in air to form hydroxides and carbonates, respectively, thus complicating sol-gel processes. Normally, all procedures have to be carried out under an inert atmosphere (nitrogen or argon) to avoid the complication. Recently, it was found that the modification of a metal alkoxide to an M(OR)_x(OAc)_y type species, where R is an alkyl, OAc is an acetate group and x and y depend on the ratio of metal alkoxide and acetic acid, dramatically improves the stability of the precursor solutions [9]. The operations can be carried out under ambient conditions instead of under an inert atmosphere. We can treat metal alkoxides with glacial acetic acid to obtain acetoxylated precursors. This technique is very important as it can greatly lower the processing costs, especially for commercial applications. It can also help to circumvent the problem of premature hydrolysis of metal alkoxide precursors since under acidic conditions the hydrolyzed acetoxy type precursors can dissolve in excess water, thus making it possible to keep the precursor solutions for a long time without degradation.

Preparation of 20% Y₂O₃-80% ZrO₂ precursor dipping solution

1. A glove bag was set up under nitrogen atmosphere. Forty-eight grams of Zr butoxide (80% in butanol), which contains 0.1 mol of Zr, was dissolved in 57 ml of isopropanol in the glove bag. Yttrium isopropoxide (7.7 g of 95% Yttrium isopropoxide) was weighed and transferred into the reaction vessel. The total volume of the solution was about 200 mL.
2. The solution was refluxed for 2 h under nitrogen. After cooling down to room temperature, 76.7 g of acetic acid (10 times of the amount of Y and Zr) was added dropwise through an addition funnel. Acetic acid was added to acetoxylate some of

the alkoxyl groups so that the dipping can be carried out in air instead of under an inert atmosphere. The resultant solution was refluxed for 2 h under nitrogen.

3. After the reaction vessel was cooled down to room temperature, water was added dropwise. A precipitate formed and re-dissolved upon adding more water. The total volume of water added was 180 mL (a fairly clear solution was obtained with addition of about 100 mL of water, but excess water was added).
4. The total amount of the solution was 553 mL, which was the yttria-stabilized zirconia (YSZ) precursor solution, **Dipping Solution 1**.

Preparation of ZrSiO_4 dipping solution

1. Partial hydrolysis of tetraethyl orthosilicate (TEOS): 20.8 g (0.1 mole) of TEOS was dissolved in 300 mL of isopropanol, and 2.4 ml of water (0.13 mol, 1/3 equivalent of -OEt group) was added into the solution for hydrolysis. A few drops of 1.0 N nitric acid were added as catalyst. The solution (1) was warmed (40-50 °C) for three hours.
2. Preparation of Zr butoxide isopropanol solution: A glove bag was set up under nitrogen atmosphere. Forty-eight grams of Zr butoxide (80% in butanol), which contains 0.1 mol of Zr, was dissolved in 57 ml of isopropanol in the glove bag. The total volume was 100 mL (2). The reaction vessel was sealed under nitrogen and taken out of the glove bag.
3. The partially hydrolyzed isopropanol solution of TEOS (1) was added into the isopropanol solution of Zr butoxide (2) through an addition funnel under nitrogen. The resulting solution was refluxed for 2 h.
4. After cooling down to room temperature, 120 g of acetic acid (10 times excess relative to the amount of Zr and Si) was added dropwise into the solution through the addition funnel. Acetic acid was added to acetoxylate some of the ethoxyl groups so that the dipping can be carried out in air instead of under an inert atmosphere. The resultant solution was refluxed for 2 h under nitrogen.
5. After the reaction vessel was cooled down to room temperature, water was added dropwise. The solution became cloudy. Water was added continuously until a clear solution was obtained. The total volume of water was 80 mL.
6. The total amount of the solution was 538 mL, which was the ZrSiO_4 precursor solution, **Dipping Solution 2**.

Coating, Heat Treatment and Characterization

The development of a bond coating is not in the scope of the current investigation. However, pre-treating the bond coated substrate is a necessary step for further coating. The compositions of the bond coating are typically selected to form a stable alumina scale, which will be the final defense against oxidation, and it will also provide a suitable bond surface for the zirconia.

In this Phase I effort, three kinds of bond coated superalloys were used:

- 2 pin samples of IN 738 (3.5" x 1/4" ϕ) coated on one side with a NiCoCrAlY HVOF (High Velocity Oxygen Fuel) bond coat (similar to EBPVD TBC coating).
- 2 flat samples of IN738 (1" x 1/2" x 1/8") coated on one side with a NiCoCrAlY HVOF (High Velocity Oxygen Fuel) bond coat (similar to EBPVD TBC coating).
- 2 flat samples of IN738 (1" x 1/2" x 1/8") coated on one side with a NiCoCrAlY plasma bond coat.

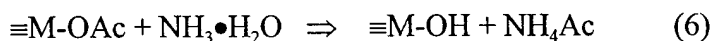
The substrates are all IN 738, and the bond coating composition is a NiCoCrAlY of GT-33/ATD 61 type.

Pin sample

The SEM pictures of the superalloy substrate and the bond coat are given in Figures 5 and 6, respectively. Thermal oxidation was used to generate the adherent Al_2O_3 scale, prior to applying the yttria-stabilized zirconia (YSZ) coatings. The bond-coated superalloy was heated in air to 1100 °C for 5 hours, and the color of the bond coat changed from gray to blue, and the SEM picture of the bond coat after heat treatment is shown in Figure 7. Spherical Al_2O_3 particles were formed, and this alumina layer provides oxidation protection to the underlying substrate.

The pretreated substrates were dipped in the YSZ precursor solution (dipping solution 1) and withdrawn at a constant slow rate. The "as synthesized" solution was used first, but was found to be too dilute. The concentrated solutions were used in all other experiments by reducing the volume of the dipping solutions to 1/10 of the original. The coated substrates were exposed to ammonia vapor overnight to facilitate development of the film.

The $\text{M(OR)}_x(\text{OAc})_y$ type species in dipping solutions are quite stable. The addition of water to this precursor causes the hydrolysis of the alkoxy groups at a rate faster than the hydrolysis of the acetate groups. This hydrolyzed metal acetoxo type precursor $\text{M(OH)}_a(\text{OAc})_b$ is soluble in excess water. When exposed to ammonia, the acetate groups in $\text{M(OH)}_a(\text{OAc})_b$ are substituted by hydroxyl groups.



The condensation reactions (equations 2 and 3) are relatively fast, and a three-dimensional network is then formed.

The coated substrates were then heat-treated in air to 600 °C with a rate of 1 °C per minute. The samples were held at 600 °C for 1 hour and then cooled to room temperature. The SEM picture of the sample is given in Figure 8. The resulting YSZ layer consisted of blocks of YSZ from 1 or 2 μm to over 20 μm . The porous structure

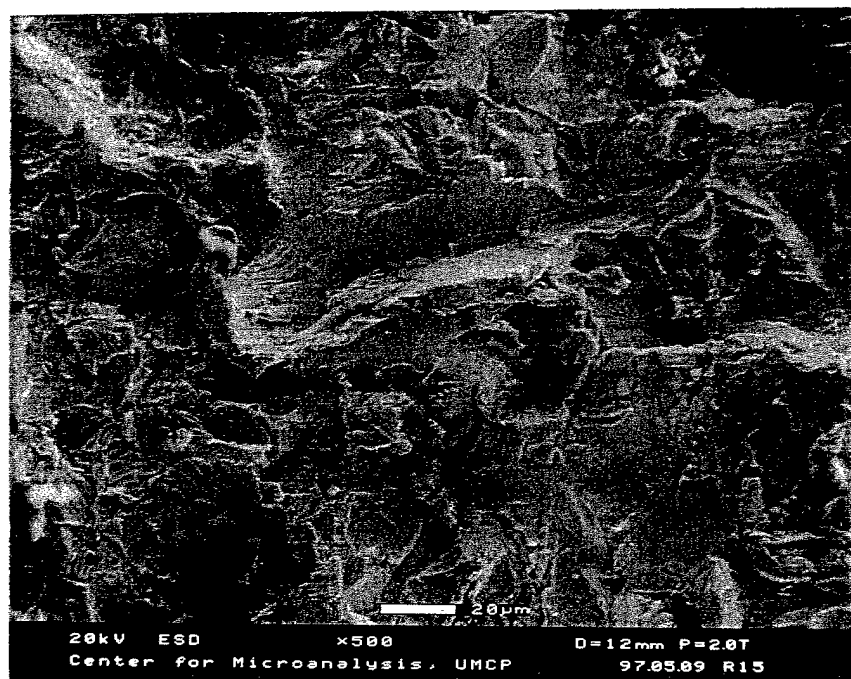


Figure 5. SEM micrograph of the superalloy substrate (pin sample) without any treatment (magnification 500).

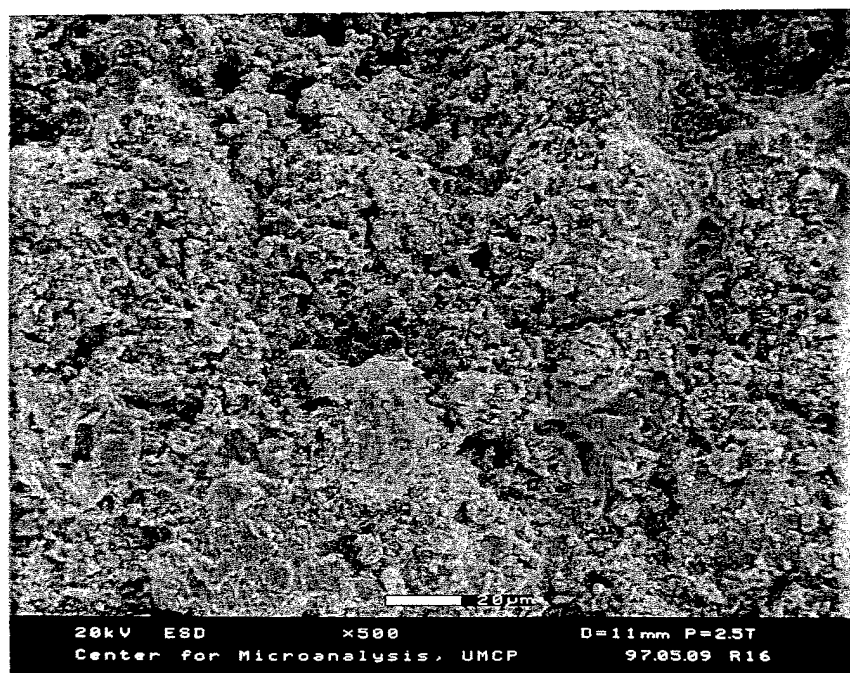


Figure 6. SEM micrograph of the bond coat of the pin sample prior to any treatment (magnification 500).

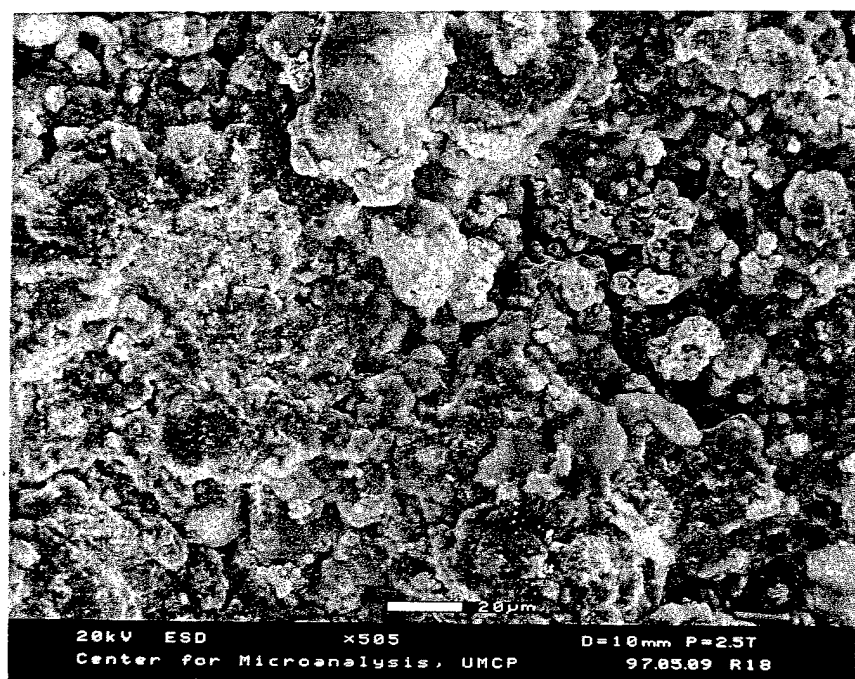


Figure 7. SEM micrograph of the bond coat (pin sample) after heat treatment at

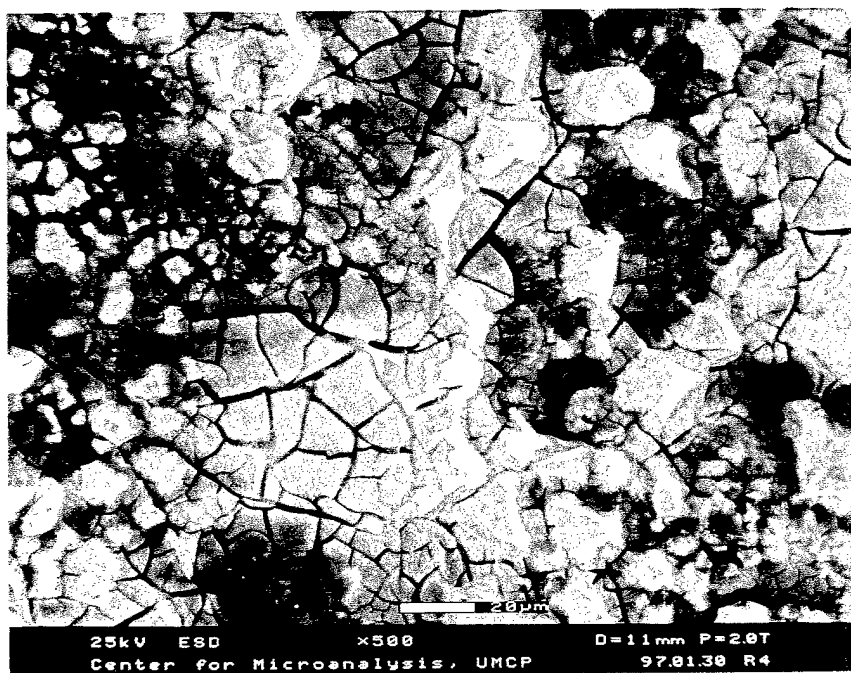


Figure 8. SEM micrograph of the YSZ film (pin sample) after heat treatment at 600 °C (magnification 500).

should provide good insulation. The thickness of the film was estimated about 1 to 2 μm , confirmed by micrometer measurement.

Flat sample with HVOF bond coat

As the yttria-stabilized zirconia (YSZ) layer is porous, oxygen can easily penetrate through the layer. The formation of Al_2O_3 scale and the YSZ can theoretically be accomplished simultaneously, which will reduce the processing cost. An experiment was carried out to verify the idea. The substrate was dip coated with the YSZ precursor solution (dipping solution 1) and heat-treated to 1100 $^{\circ}\text{C}$ in air with a rate of 5 $^{\circ}\text{C}$ per minute. The sample was held at 1100 $^{\circ}\text{C}$ for 1.5 h and cooled to room temperature. The uncoated part of the bond coat developed an Al_2O_3 scale, while the coated part developed a YSZ film. The SEM picture of the flat HVOF bond coat is given in Figure 9. The SEM pictures of the flat HVOF sample after heat treatment to 1100 $^{\circ}\text{C}$ without and with the YSZ coating are given in Figures 10 and 11, respectively.

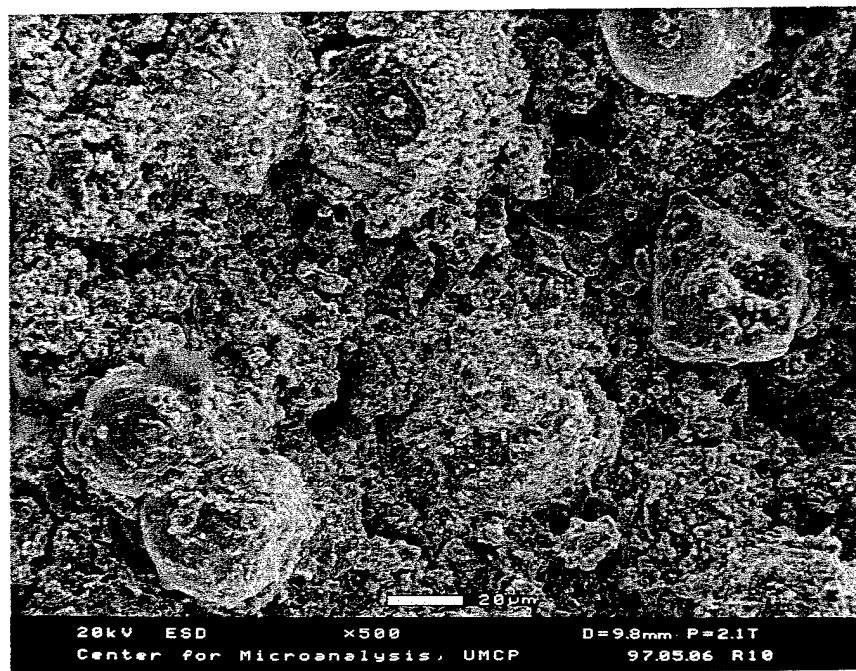


Figure 9. SEM micrograph of the HVOF bond coat without any treatment (magnification 500).

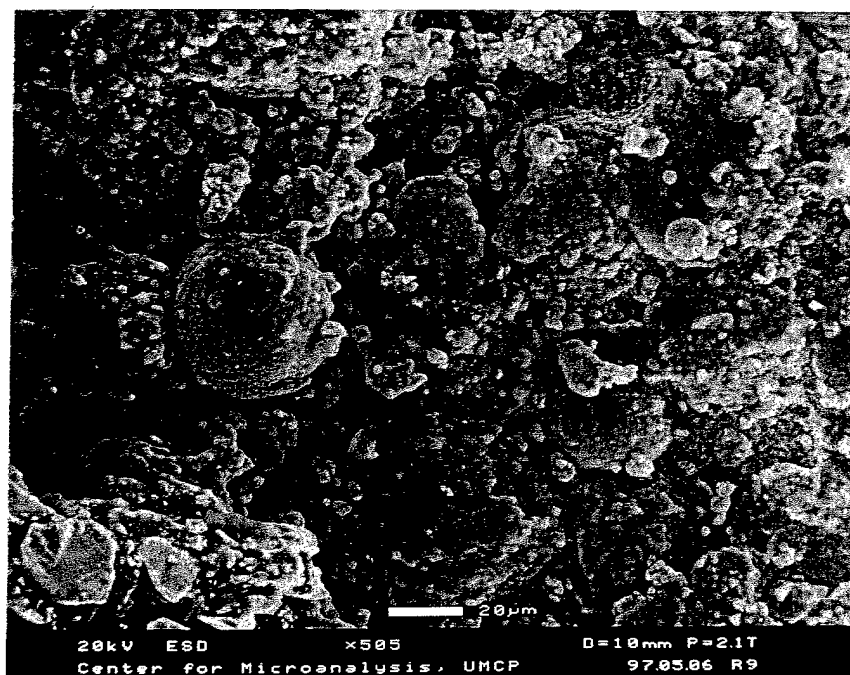


Figure 10. SEM micrograph of the flat HVOF bond coat after heat treatment to 1100 °C (magnification 500).

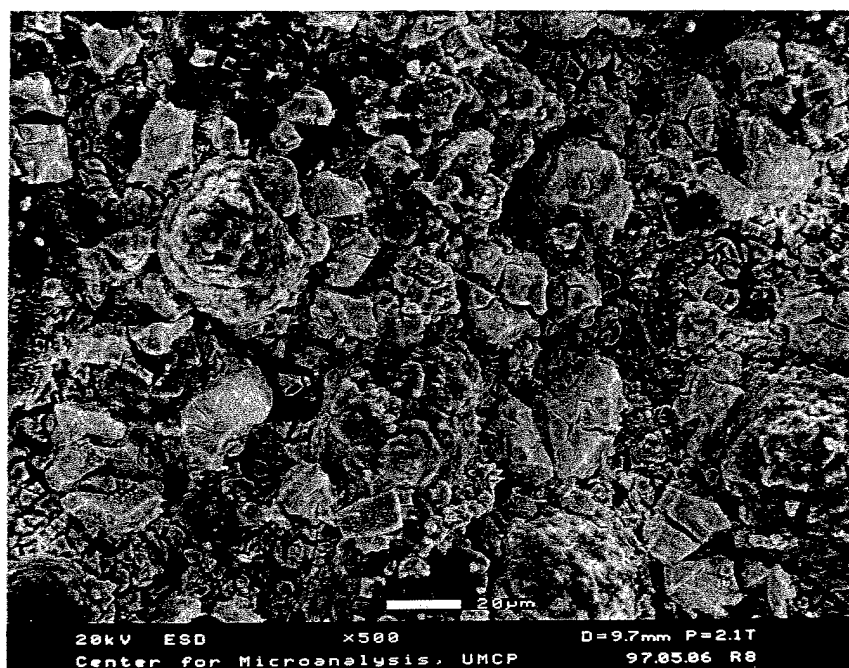


Figure 11. SEM micrograph of the YSZ film (flat HVOF sample) after heat treatment to 1100 °C (magnification 500).

Zirconia (ZrO_2) is polymorphic and undergoes two phase transitions, cubic to tetragonal at 2350 °C and tetragonal to monoclinic at 1170 °C. The latter transformation is accompanied by a 5% volume increase, which means that ZrO_2 has to be alloyed to stabilize one of the high temperature phases. An APD1700 Automated Powder Diffractometer with Cu radiation operated at 45 kV and 30 mA was used to identify the phase of YSZ films. The recorded XRD pattern is given in Figure 12. The observed peak intensity and position together with standard patterns of cubic zirconia ($a = 4.620 \text{ \AA}$, space group = Fm3m, labeled ZrO_2 27-997), two tetragonal zirconia ($a = 3.640 \text{ \AA}$, $c = 7.270 \text{ \AA}$, labeled ZrO_2 24-1164; $a = 5.120 \text{ \AA}$, $c = 5.250 \text{ \AA}$, labeled ZrO_2 17-923) are given in Figure 13. The coated film was clearly cubic zirconia, and the thickness was estimated to be 1-2 μm .

Flat sample with plasma bond coat

The superalloy sample with plasma bond coat was heat-treated to 1100 °C with a rate of 5 °C per minute. The sample was held at 1100 °C for 2 h and cooled to room temperature. The SEM picture of the alumina scale is given in Figure 14. The substrate was dip coated with the YSZ precursor solution (dipping solution 1) and exposed to ammonia overnight. The substrate was then heat-treated to 500 °C, which was enough for crystallization (Figure 15). The substrate was then dip coated with ZrSiO_4 precursor solution (dipping solution 2) and exposed to ammonia. The substrate was then again heat-treated to 500 °C, and a glassy phase of ZrSiO_4 was formed (Figure 16). The substrate was then coated with the dipping solution 1 again and exposed to ammonia overnight. After heat treatment to 500 °C, a zirconia film was formed (Figure 17). The APD1700 Automated Powder Diffractometer with Cu radiation operated at 45 kV and 30 mA was also used to identify the phase of YSZ films after 3rd coating. The recorded XRD spectrum is given in Figure 18. The observed peak intensity and position together with standard patterns of cubic zirconia ($a = 4.620 \text{ \AA}$, space group = Fm3m, labeled ZrO_2 27-997), two tetragonal zirconia ($a = 3.640 \text{ \AA}$, $c = 7.270 \text{ \AA}$, labeled ZrO_2 24-1164; $a = 5.120 \text{ \AA}$, $c = 5.250 \text{ \AA}$, labeled ZrO_2 17-923) are given in Figure 19. Cubic zirconia is clearly seen in the observed pattern, but the highest peak is due to the substrate, indicating high temperature heating does help crystallization of cubic zirconia.

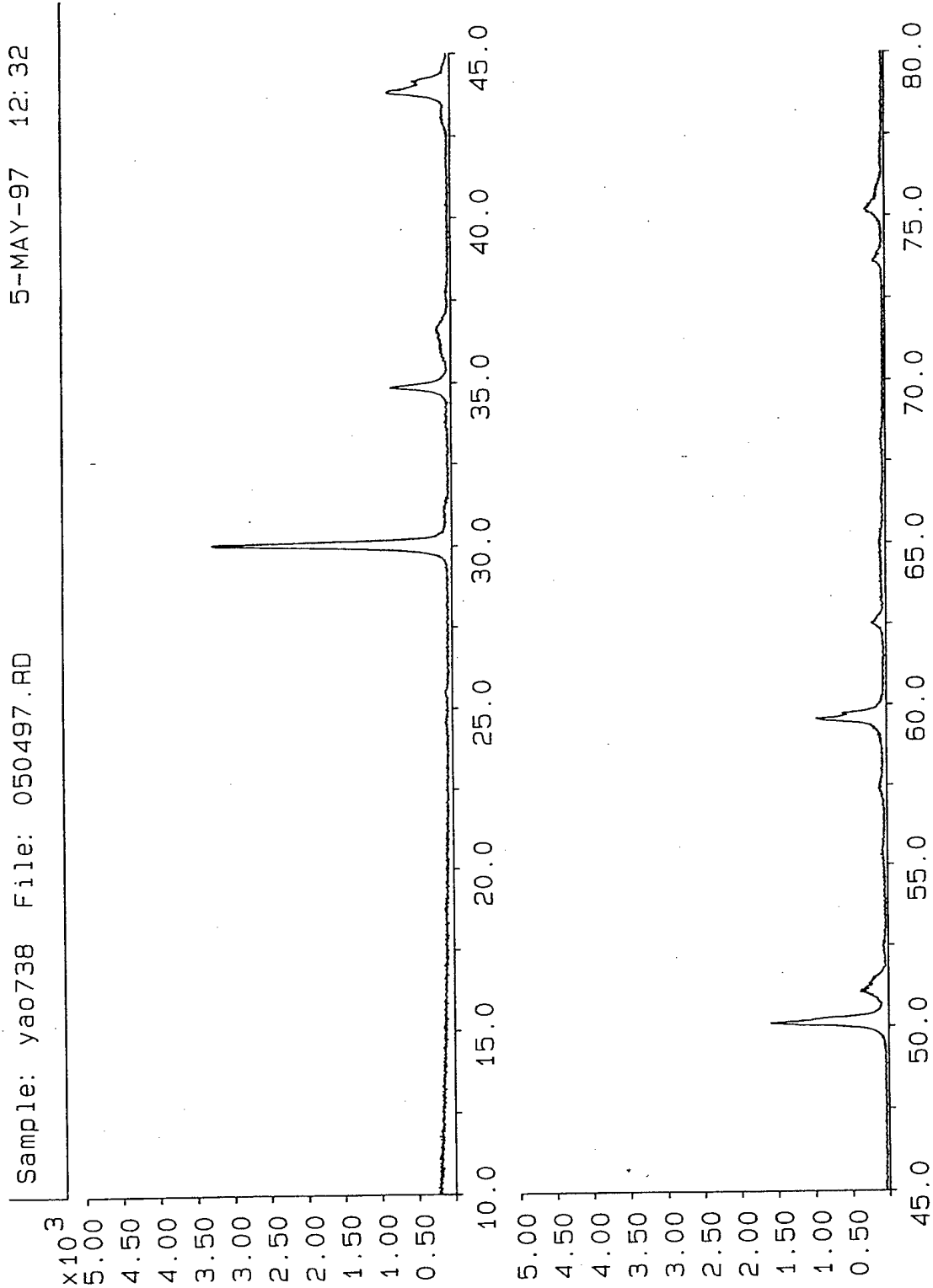


Figure 12. XRD pattern of the YSZ film (HVOF bond coat) after heat treatment at 1100 °C.

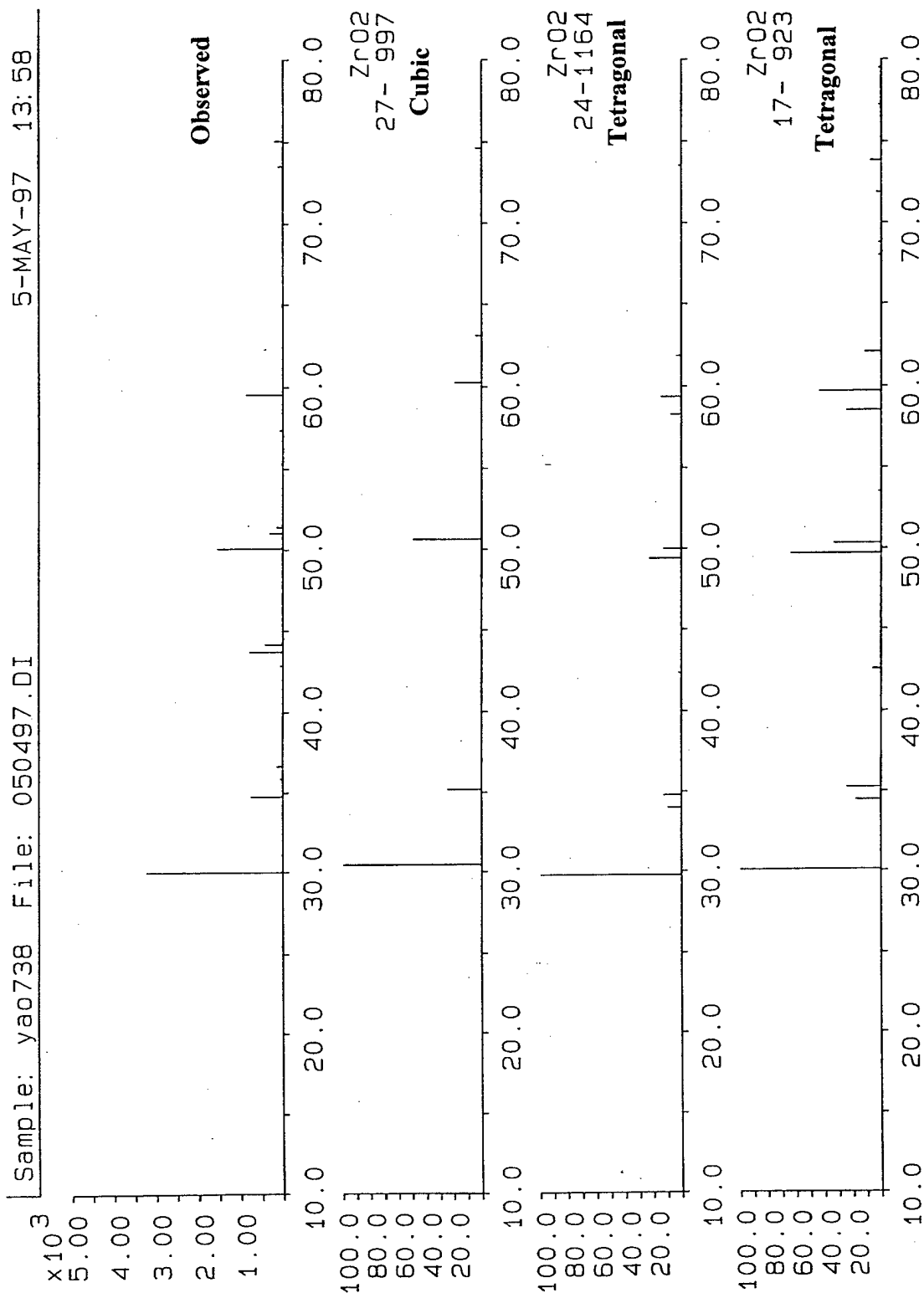


Figure 13. XRD patterns of the YSZ film (HVOF bond coat) after heat treatment at 1100 °C and some standard zirconia.

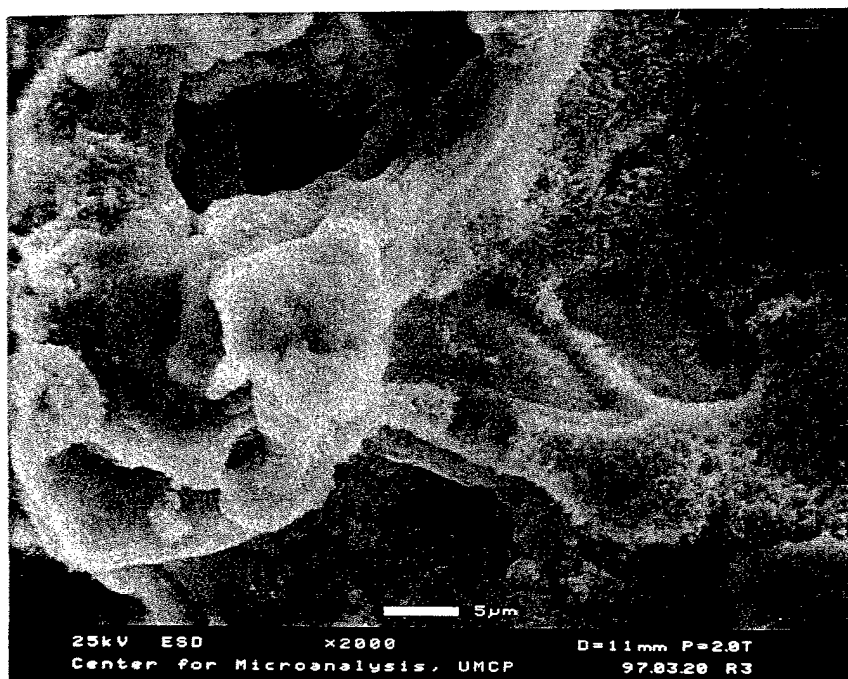


Figure 14. SEM micrograph of the plasma bond coat after heat treatment at 1100 °C (magnification 2000).

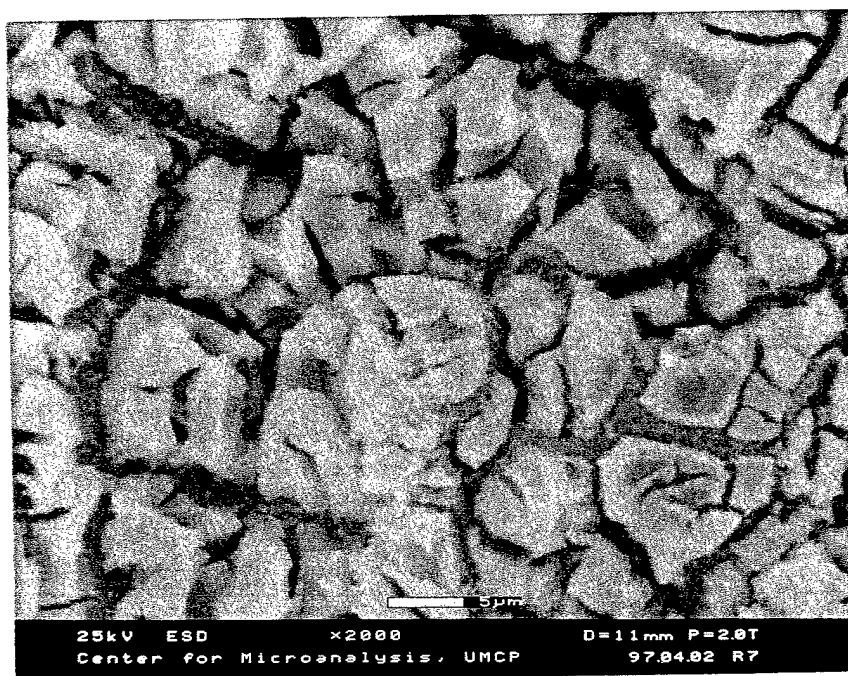


Figure 15. SEM micrograph of the YSZ film (plasma bond coat) heated to 500 °C after 1st coating (magnification 2000).

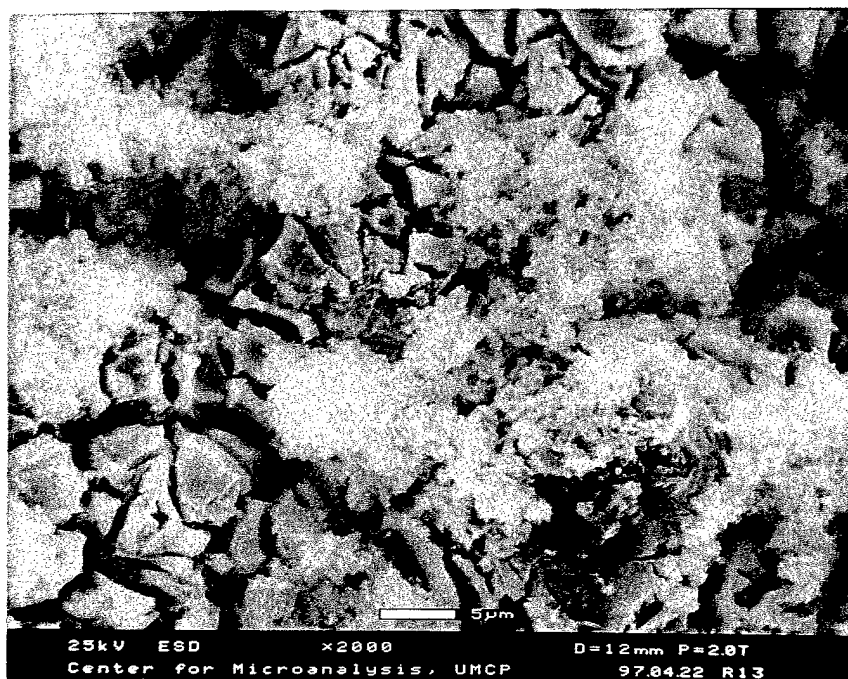


Figure 16. SEM micrograph of the ZrSiO_4 film (plasma bond coat) after heat treatment to 500 °C after 2nd coating (magnification 2000).

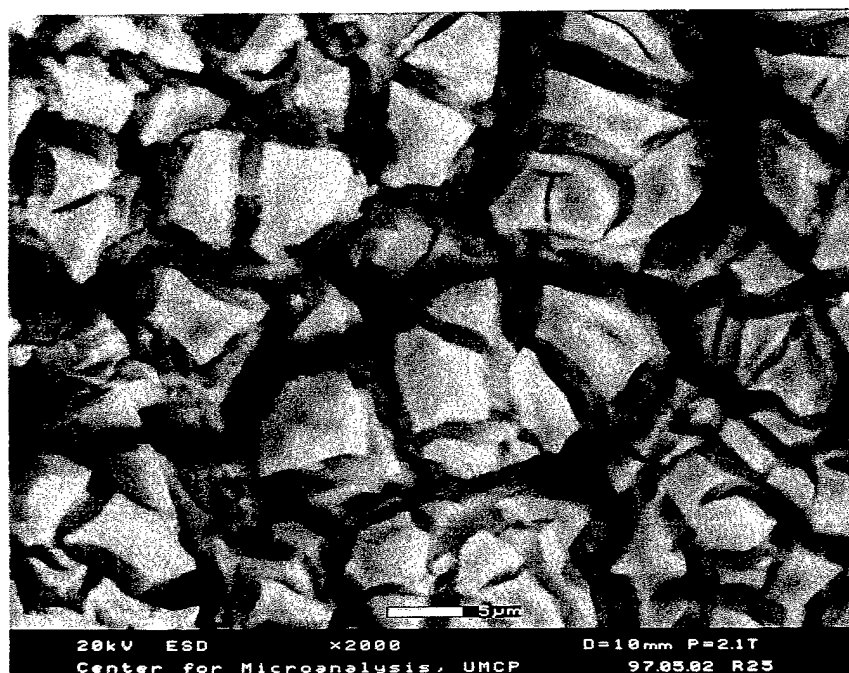


Figure 17. SEM micrograph of the YSZ film (plasma bond coat) after heat treatment to 500 °C after 3rd coating (magnification 2000).

Sample: yao428 File: 042897.RD 5-MAY-97 12:31

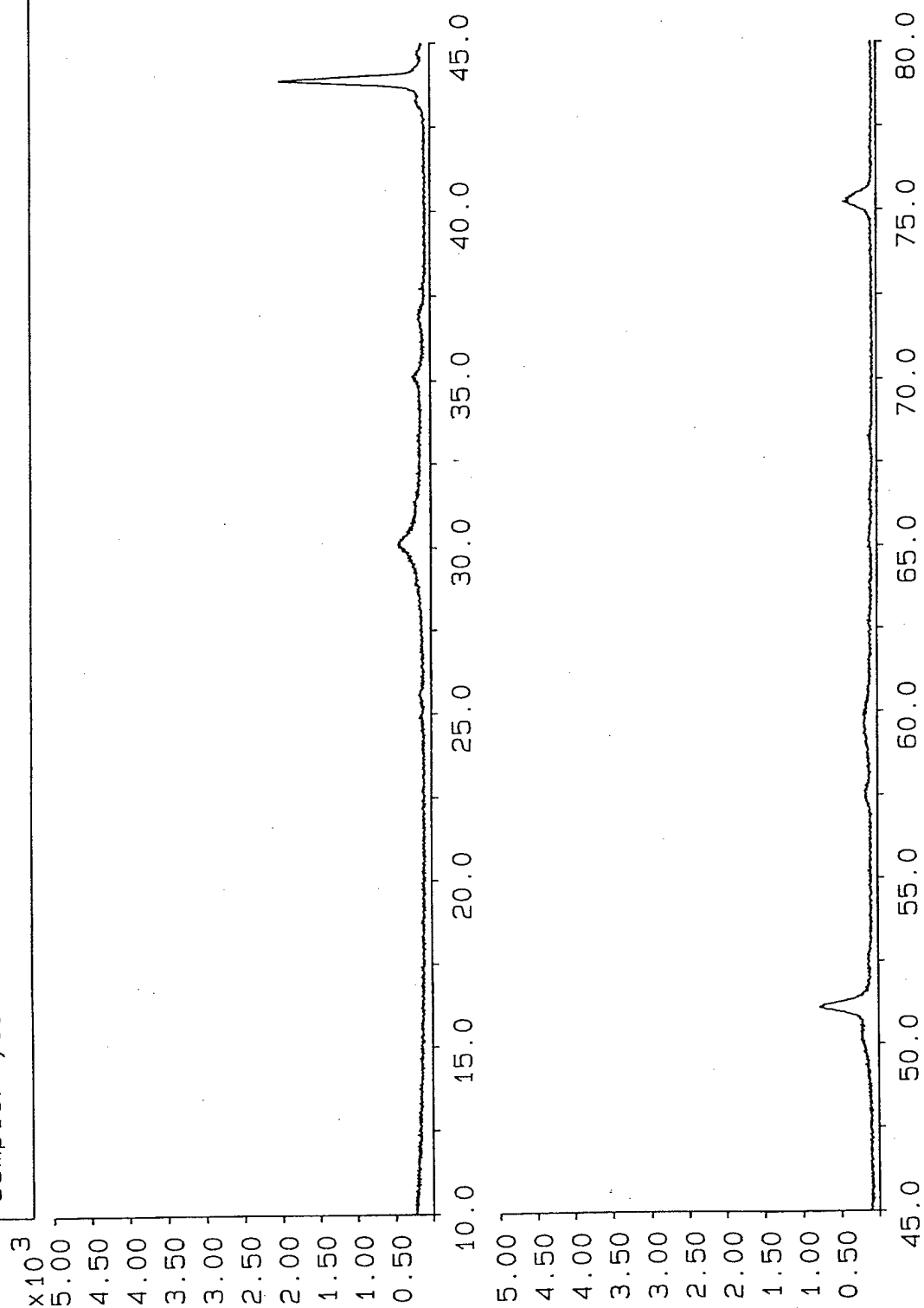


Figure 18. XRD pattern of the YSZ film (plasma bond coat) after 3rd coating (heat treatment at 500 °C).

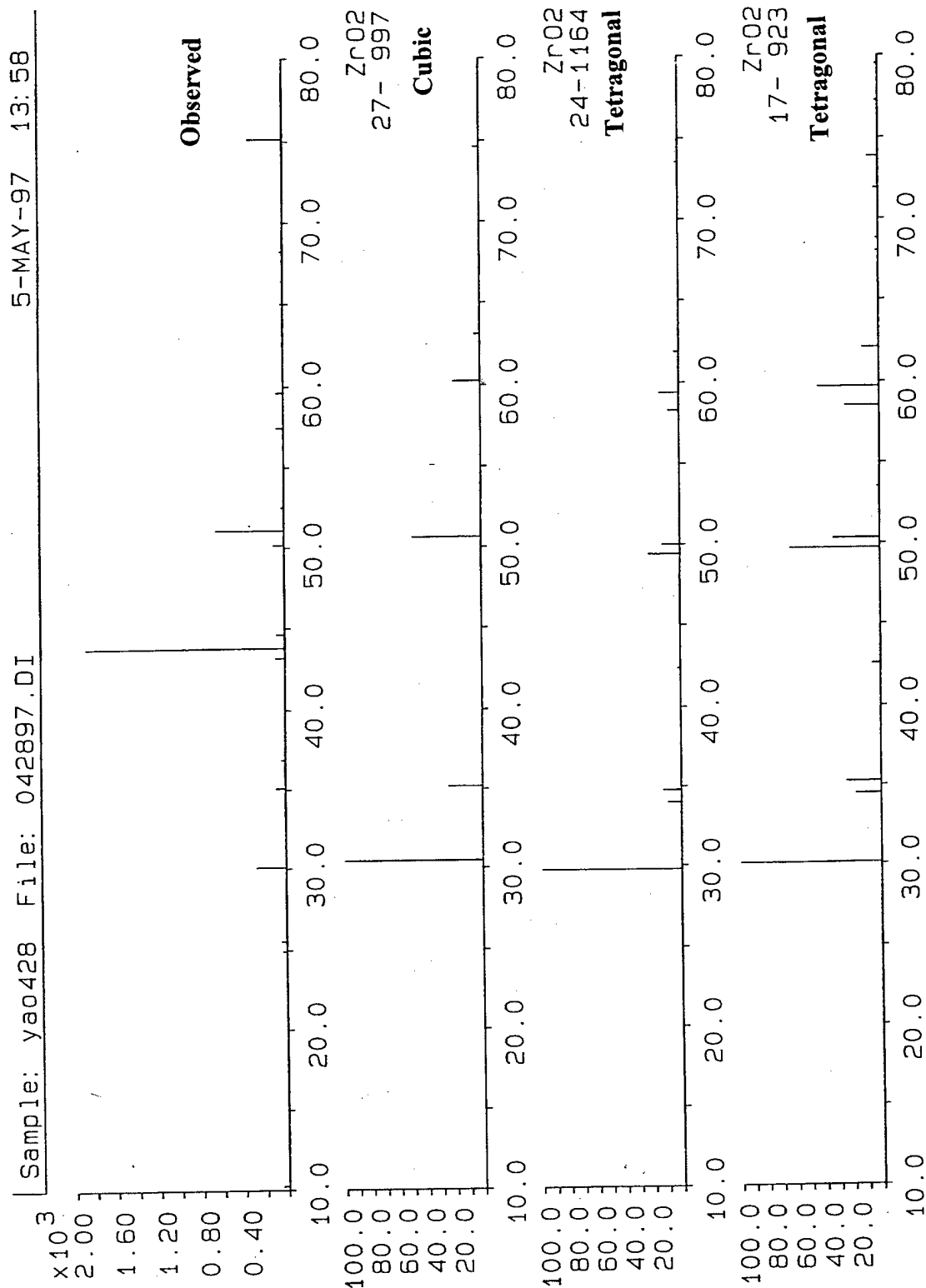


Figure 19. XRD patterns of the YSZ film (plasma bond coat) after 3rd coating (heat treatment 500 °C) and some standard zirconia.

4.0 Conclusions

This Phase I has demonstrated clearly the following:

- Cubic zirconia (yttria-stabilized-zirconia) can be coated through a sol-gel process onto bond coated superalloys. The films have very good adhesion and cohesion demonstrated by tape test. The films on the other side of the superalloy without bond coat peeled off very easily.
- Zircon (ZrSiO_4) can be coated onto the yttria-stabilized-zirconia (YSZ) layer as a reinforcement layer. The glassy phase may help to relieve the stress during thermal cycling.
- Cubic zirconia (yttria-stabilized-zirconia) can be coated onto the zircon layer. The feasibility of applying multilayer thermal barrier coating with micro-laminated structure through a sol-gel approach has been clearly demonstrated.
- The cubic zirconia films are stable at 1100 °C, which is close to the service temperatures of a turbine engine. The crystallization of the cubic zirconia can be achieved at 500 °C.
- All the objectives stated in the Phase I effort have been thus successfully completed.

Plans for Phase II

The development of this unique multilayer thermal barrier coating with micro-laminated structures through a sol-gel process has the potential to increase turbine-operating temperatures, reduce costs, and increase reliability. Even small increases in operating temperatures yield big payoffs in turbine performance, efficiency, and pollution reduction. The sol-gel process is very flexible for applications, and coatings can be applied through dip coating, spray coating, spin coating, roller coating, and brushing coating. It will be especially suitable for parts with complex geometry.

The experiences gained and the feedback obtained from the Phase I effort will be used as guidelines for further formulation refinement, process improvement, and product commercialization during Phase II.

In Phase II, we will concentrate on optimization of the formulation, coating procedure and post treatment. Different coating techniques mentioned above will be used. Extended tests of coating characteristics will be carried out. A new laser technique will be used to measure insulation of the films.

The feedback from the tests will be used to improve coating performance by microstructural modification such as sequence, thickness and porosity of the laminates. We will also explore other materials as reinforcement and oxygen barrier layers such as TiO_2 .

We will then manufacture a prototype coated turbine blade for extended ground testing under simulated conditions. Finally the prototype will undergo testing under actual conditions.

The path from Phase I to Phase II, to commercialization will be:

- Formulation and process refinement for production
- Coating characteristic evaluation
- Further improvement of formulation/process parameters based on evaluation feedback
- Prototype manufacturing and testing
- Analysis/identification/awareness of the strength/weakness of existing production process and competitors
- Demonstration of superior properties of our processes/products
- Patent rights
- Identification of markets for our products
- Detailed analysis of the potential for payoff
- Economics of scale-up of materials/equipment/personnel for large scale production
- Schematics of day to day operation
- Infrastructure build-up
- Development of marketing data.

Applications

The direct application of the technology developed in this SBIR effort will be multilayer, micro-laminated thermal barrier coatings on gas turbine components for high efficiency engines. This technology can also be used in a wide range of industries where protective coatings against corrosion and erosion for components used under severe conditions are essential. Other commercial applications include:

- scramjet and ramjet turbine component,
- reusable heat shields for reentry vehicle nosecones,
- flame nozzles
- water jet nozzles.

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This effort is funded by the Air Force Small Business Innovation Research Program.